

## Atomic Structure

### DALTON'S THEORY OF ATOM

### SECTION - 1A

**John Dalton** developed his famous theory of atom in 1803. The main postulates of his theory were :

- Atom was considered as a hard, dense and smallest indivisible particle of matter.
- Each element consists of a particular kind of atoms.
- The properties of elements differ because of differences in the kinds of atoms contained in them.
- This theory provides a satisfactory basis for the law of chemical combination.
- Atom is indestructible, i.e., it cannot be destroyed or created.

#### Drawbacks

- It fails to explain why atoms of different kinds should differ in mass and valency etc.
- The discovery of *isotopes* and *isobars* showed that atoms of same elements may have different atomic masses (*isotopes*) and atoms of different kinds may have same atomic masses (*isobars*).
- The discovery of various sub-atomic particles like X-rays, electrons, protons etc. during late 19th century lead to the idea that the atom was no longer an indivisible and smallest particle of the matter.

### DISCOVERY OF CATHODE RAYS & POSITIVE RAYS

### SECTION - 1B

#### Cathode Rays

**Sir William Crooks** studied various gases in a *gas discharge tube* (a glass tube with a very high potential applied to its ends) at low pressures. If the pressure in the tube is lowered to about  $10^{-4}$  atm, glass begins to fluoresce (glow) faintly. It was established that the glow was due to bombardment of the glass by a certain kind of rays emerging from **cathode** (negative electrode) which travel in a straight line until they strike the **anode** (positive electrode). These rays were called as *cathode rays*.

**Sir J. J. Thomson** demonstrated that when cathode rays were deflected on to an electrometer, it acquired negative charge. He also showed that the rays were deflected on application of an electric field. The cathode ray beam was deflected away from the negatively charged plate. These results were found to be identical, irrespective of the gas taken in the discharge tube. He concluded that the cathode rays were a stream of fast moving negatively charged particles called **electrons** (named by **Stoney**). He also calculated the velocity and specific charge for an electron. The *specific charge* is the ratio of charge to the mass of an electron, denoted as **e/m** ratio. The **e/m** ratio was found to be same for all gases. This led to the conclusion that the electron must be a fundamental or universal particle common to all kinds of the atoms. The **e/m ratio** (for an electron) =  $1.758 \times 10^{11}$  C/Kg.

- Note:** (i) **J. Millikan** determined the value of the charge on an electron with the help of famous *Oil drop experiment*. The magnitude of the charge on an electron =  $1.60206 \times 10^{-19}$  C and the mass of an electron =  $9.1 \times 10^{-31}$  kg.
- (ii) You will be studying the details of Thomson's calculations of e/m ratio and Millikan's oil drop experiment for the determination of electronic charge later in *Modern Physics* in the Module of Physics.

**Positive Rays**

Since the atom as a whole is neutral, it means that an equal amount of positive charged particle should also be there in the atom. **Goldstein**, by carefully experimenting with the discharge tube consisting of perforated cathode, showed the presence of another type of rays. These rays emanating from anode passed through the perforations in the cathode. These carried *positive* charge and were called as *positive or anode rays*. It was established that these rays consist of *positively* charged particles called as **protons**. The magnitude of charge on a proton is same as that on an electron, but its mass was found to be 1837 times the mass of an electron. The mass of a proton =  $1.6735 \times 10^{-27}$  kg.

Since the electron has negligible mass (as compared to the proton), so it was assumed that whole mass of an atom is associated with the protons. Later in 1932, with the discovery of **neutron** as IIIrd fundamental particle (*Ist and IInd being electron and proton*), it was established that the mass of an atom is the total mass of protons and neutrons taken together.

**Important Facts**

1. Mass of Proton =  $1.672623 \times 10^{-27}$  kg or 1.007276 u and charge on the proton is  $+1.6022 \times 10^{-19}$  Coulomb  
The  $\frac{e}{m}$  ratio value for proton is  $9.578 \times 10^4$  C / g . Also,  $mass_{proton} \approx 1837 \times mass_{electron}$
2. Mass of Neutron =  $1.674929 \times 10^{-27}$  kg or 1.008664u. The neutron is charge-less. The neutron was discovered by Sir James Chadwick. He bombarded  $\alpha$  -particles on a beryllium nucleus ( $Be_4^9 + He_2^4 \rightarrow C_6^{12} + {}_0^1n$ ) to obtain a stable carbon-12 isotope along with a neutron.
3. It has been revealed that nucleus has a diameter of the order of  $10^{-15}$  m while the atom has a diameter of the order of  $10^{-10}$  m.
4. **ISOTOPES**: These are those variants of an element that differ in their number of neutrons. For instance,  ${}^{12}_6C$ ,  ${}^{13}_6C$  and  ${}^{14}_6C$  constitute different isotopes of Carbon
5. **ISOBARS**: These are atoms (nuclides) of different chemical elements that have the same number of nucleons. Correspondingly, isobars differ in atomic number (or number of protons) but have the same mass number. An example of a series of isobars would be  ${}^{40}_{16}S$ ,  ${}^{40}_{17}Cl$ ,  ${}^{40}_{18}Ar$ ,  ${}^{40}_{19}K$ , and  ${}^{40}_{20}Ca$ . The nuclei of these nuclides all contain 40 nucleons; however, they contain varying numbers of protons and neutrons.
6. **ISOTONES**: Two nuclides are isotones if they have the same neutron number N, but different proton number Z. For example, boron-12 and carbon-13 nuclei both contain 7 neutrons, and so are isotones. Similarly,  ${}^{36}_{16}S$ ,  ${}^{37}_{17}Cl$ ,  ${}^{38}_{18}Ar$ ,  ${}^{39}_{19}K$ , and  ${}^{40}_{20}Ca$  nuclei are all isotones of 20 because they all contain 20 neutrons.
7. **MAGIC NUMBERS**: It has been observed that stable nuclei result when either neutrons or protons are one of the numbers 2, 8, 20, 28, 50, 82 and 126. These are considered to be magic numbers.

**MODELS OF ATOM****SECTION - 2A****Thomson's Model**

Putting together all the facts known at that time, Thomson assumed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere. This was known as *plum-pudding model* at that time. However this idea was dropped due to the success of  $\alpha$ -scattering experiments studied by **Rutherford and Mardson**.

### Rutherford's Model

Rutherford studied the scattering of  $\alpha$  particles (doubly ionised Helium atom) by the thin metallic foils (of gold, platinum etc.). A narrow pencil beam of fast moving  $\alpha$  - particles were struck on a thin metal foil ( $\approx 10^4$  atoms thick). The angular deflections of scattered  $\alpha$  particles were studied with the help of a moving microscope.

#### Observations of the Rutherford's experiment :

- Most of the  $\alpha$ -particles passed through the foil undeflected, i.e., went straight through the foil.
- Some of them were deflected, but only at small angles.
- A very few (1 in 20,000) were deflected at large angles ( $\approx 180^\circ$ ).

#### Conclusions :

- As most of the  $\alpha$ -particles passed undeflected, it was concluded by Rutherford that the atom must be predominantly empty.
- $\alpha$ -Particles are positively charged with appreciable mass (4 amu) and were moving high kinetic energy. In order to produce deflections, there must be some enormous positively charged body inside the atom.
- Only a few received large deflections. This led to the conclusion that enormous charge must be confined to a very small region. This small region was given the name **nucleus**.
- Rutherford then proposed that an atom is composed of a dense positive nucleus, thinly surrounded by the electrons. The mass and the positive charge of the nucleus are confined in a very small region of space. The electrons are outside the nucleus, so that an atom is almost entirely empty space.
- From stability point of view, the electrons cannot be stationary otherwise they would be drawn into the nucleus. So Rutherford assumed that electrons were moving in circles around the nucleus; the necessary centripetal force being provided by the electrostatic attraction between nucleus and the electrons. He gave no further justification for this assumption.

- Note :**
- From experiments, it was confirmed that within the nucleus, the distribution of positive charge is uniform and atomic nuclei are spherical in shape.
  - Later with the discovery of the neutrons (In 1932 by Chadwick), it was established that these also occupy the place in the nucleus bonded along with the protons by a very complex type of forces called as *Nuclear Forces*.
  - Now the constituents of the nucleus, i.e., Protons and Neutrons are called as *Nucleons* and the number of nucleons in a particular atom is called as *Mass Number* denoted by **A**. The number of protons is known as *Atomic Number* denoted by **Z**.
  - The order of the diameter of an atom is  $10^{-10}$  m or  $1 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10}$  m) and the order of the diameter of the nucleus is  $10^{-15}$  m or  $1 \text{ fm}$  (*fm* is called as Fermi and  $1 \text{ fm} = 10^{-15}$  m).
  - Radius of the nucleus of an atom is proportional to the cube root of the mass number of an atom (i.e., the number of nucleons in the atom). If  $r_0$  denotes the radius of the nucleus then,  
$$r_0 = (1.2 \times 10^{-15}) A^{1/3} \text{ m.} \quad (A = \text{mass number})$$

### Failure of Rutherford's Model

According to *Classical Theory of Electromagnetism*, whenever a charge is subjected to acceleration around an opposite charge, it emits radiation continuously. Hence the electron in Rutherford's atom will lose energy and will not be able to stay in a circular path around the nucleus and should ultimately go into a spiral motion. Such an electron will fall into the nucleus. This, of course, does not happen for electrons in an atom and the discrepancy could not be explained at that time.

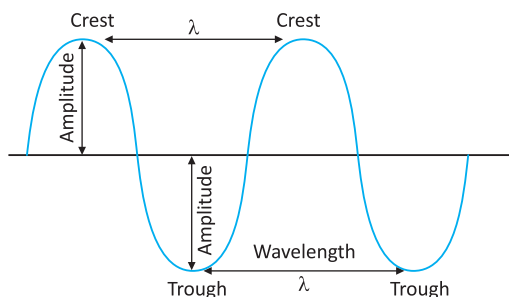
**Note:** Later Niel Bohr, a student of Rutherford analysed atomic spectra of Hydrogen atom in terms of *Quantum Theory of Radiation* and applied the results of *Photoelectric Effect* to it and developed a model of atom which was widely accepted at that time.

## NATURE OF CHARACTERISTICS OF RADIANT ENERGY

## SECTION - 2B

**Newton** was first person to comment on the nature of light in terms of *Corpuscular Theory of Light*. According to this theory, light is a stream of particles commonly known as *corpuscles of light*. He was able to explain *reflection* and *refraction*, the most common phenomenon of light. But the other phenomenon like *diffraction* and *interference* could not be explained on the basis of this theory.

**Maxwell**, in 1865 proposed that radiant energy (light) has wave characteristics. Light according to him is *Electromagnetic Wave* arising due to the disturbance created by electric and magnetic fields oscillating perpendicular to each other in space. Like all other mechanical waves, it is characterised by velocity,  $c$ ; frequency,  $\nu$  and wavelength,  $\lambda$  which are related as :



Characteristics of wave

- **Wavelength ( $\lambda$ ):** The distance between two nearest, crests or troughs is known as wavelength. It is expressed in meters, picometers (pm), nanometers (nm) or Angstrom ( $\text{\AA}$ ) units ( $1 \text{ pm} = 10^{-3} \text{ nm} = 10^{-2} \text{ \AA} = 10^{-10} \text{ cm} = 10^{-12} \text{ m}$ ).
- **Frequency ( $\nu$ ):** The number of times a wave passes a given point in one second is known as frequency of the wave. It is expressed in Hz (hertz) or cps (cycles per second) unit ( $1 \text{ Hz} = 1 \text{ cps}$ ).
- **Velocity ( $c$ ):** The distance travelled by the wave in one second is known as velocity of the wave, it is expressed in  $\text{ms}^{-1}$  and related to  $\nu$  as:  $c = \nu \lambda$  [value of  $c$  is constant and equal to  $3 \times 10^8 \text{ m/s}$ ] or  $\nu = \frac{c}{\lambda}$  ... (i)
- **Wave number ( $\bar{\nu}$ ):** It is reciprocal of wavelength i.e. the number of wavelengths per centimetre or
 

$$\bar{\nu} = \frac{1}{\lambda} \text{ m}^{-1} \quad \dots \text{(ii)}$$

$$\bar{\nu} = \frac{\nu}{c} \text{ m}^{-1} \quad \dots \text{(iii)}$$
- **Amplitude (A):** It is the height of the crest or depth of the trough of a wave. It determines the intensity (brightness) of the beam of light.

When the different types of electromagnetic radiations are arranged in the increasing or decreasing order of wavelengths or frequencies, the pattern so obtained is called an electromagnetic spectrum.

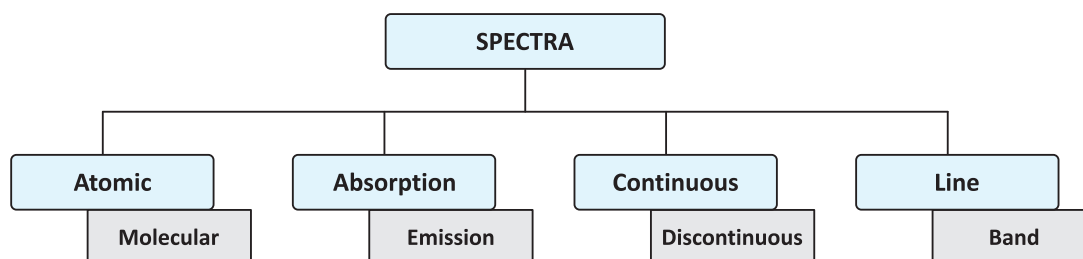


### Electromagnetic Spectrum

- Electromagnetic wave or radiation is not a single wavelength radiation, but a mixture of various wavelength or frequencies. All the frequencies have same speed ( $= c$ ).
- If all the components of *Electromagnetic Radiation* (EMR) are arranged in order of decreasing or increasing wavelengths or frequencies, the pattern obtained is known as *Electromagnetic Spectrum*. The following table shows all the components of light.

Wavelength, $\lambda$ (in Å)	0.01	1.0	150	3800	7600	$6 \times 10^6$	$3 \times 10^9$	
	Cosmic-rays	$\gamma$ rays	X-rays	UV rays	Visible light	Infra-red	Micro waves	Radio waves
Frequency, $\nu$ (in Hz)			$10^{17}$	$10^{15}$	$10^{14}$	$10^{11}$	$10^9$	

**Types of Spectra :** Spectra can be classified into various type as expressed below :



- (i) **Atomic and Molecular spectra :** Atomic spectra represents the radiation (energy emitted or absorb in space) by an atom whereas molecular spectra is associated with radiation (energy emitted or absorb in space) by a molecule. Molecular spectra is more complex than atomic spectra because molecule involve more electronic transitions than in atom.
- (ii) **Absorption spectra and emission spectra :** Absorption spectra shows the wavelengths absorbed by an atom/molecule. The wavelengths absorbed appear as lines missing from the continuous spectra of radiation to which species is exposed. Each wavelength absorbed is characteristic of energy transition taking place in that species.
- On the other hand, emission spectra indicates the wavelengths (or frequencies) emitted by an excited species. Each spectral line of emission spectra is characteristic of one electronic transition from higher energy level to a lower energy level (i.e., de-excitation). Absorption and emission spectra are complementary to each other. A line missing in absorption spectra will appear in emission spectra.
- (iii) **Continuous and discontinuous spectra :** A continuous spectra is that which contains all the wavelength lying in a particular region of spectra. e.g., VIBGYOR indicates a continuous spectra in visible region.
- On the other hand, if some wavelengths are missing and spectra contain certain wavelengths, it is called discontinuous spectra. e.g., VBYR is discontinuous spectra in which I, G & O wavelengths are missing from visible radiation.
- (iv) **Line and band spectra :** Spectra containing only one or a few lines is called line spectra. It is obtained in the spectra of those species where number of electronic transitions is less. On the other hand, spectra containing several wavelengths is wide and is called band spectra. It is complex and is shown by multiatomic species in which number of electronic transitions is more.

**Note :** Light emitted from atoms heated in a flame or excited electrically in gas discharge tube, does not contain a continuous spread of wavelengths (or frequencies). It contains only certain well-defined wavelengths (or frequencies). The spectrum pattern appears as a series of bright lines (separated by gaps of darkness) and hence called as *Line Spectrum*.

One notable feature observed is, that each element emits a characteristic spectrum, suggesting that there is direct relation between the spectrum characteristics and the internal atomic structure of an atom.

### The Quantum Theory of Radiation

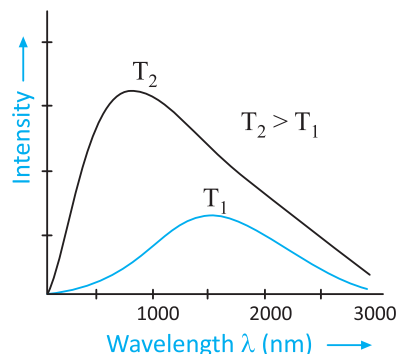
In 1901, **Max Planck** studied the distribution of the frequencies of radiations emitted from the hot bodies. He proposed a bold hypothesis that the radiant energy such as heat or light, is not emitted continuously but discontinuously in the form of small packets called as **quanta**. According to him, the energy of the electromagnetic radiation is directly proportional to the frequency of the radiation. The proportionality constant is called as *Planck's constant* ( $h$ ). If energy of the radiation is  $E$ , and the frequency of the radiation is  $\nu$ , then we have :

$$E = h \nu \quad (\text{The value of } h \text{ is } 6.626 \times 10^{-34} \text{ J-s})$$

If  $n$  is the number of quanta of a particular frequency and  $TE$  be the total energy, then :  $TE = n(h\nu)$

### BLACK BODY RADIATION (1900)

- In 1900, Max Planck was the first to give a concrete explanation for the phenomenon of black body radiation. According to the Planck's quantum theory, an ideal body is a perfect absorber and perfect emitter of radiation and called a black body.
- When such a body is heated it emits radiation over a wide range of wavelengths. For instance, when an iron rod is heated in a furnace, it firstly turns dull red, then progressively becomes more and more red as the temperature increases. On heating further, the radiation emitted becomes white and then blue as the temperature becomes very high.
- In terms of frequency, it means that radiation emitted goes from a lower frequency to higher frequency as the temperature increases. The red colour lies in the lower frequency area whereas blue light lies in the higher frequency area of the electromagnetic spectrum.
- The exact frequency distribution of emitted radiation from a black body depends only on its temperature. At a given temperature, the intensity of radiation increases with decrease in wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease in wavelength as shown in the figure below.



- Planck explained that atoms and molecules could emit (or absorb) energy only in discrete quantities (quantum) and not in an arbitrary manner as was believed at that time.

**Illustration - 1** Find the ratio of frequencies of violet light ( $\lambda_1 = 4.10 \times 10^{-5} \text{ cm}$ ) to that of red light ( $\lambda_2 = 6.56 \times 10^{-5} \text{ cm}$ ). Also determine the ratio of energies carried by them.

**SOLUTION :**

Using  $c = \nu \lambda$

where  $c$ : speed of light;  $\nu$ : frequency;  $\lambda$ : wavelength

$$\frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} \quad [1 : \text{violet and } 2 : \text{red}]$$

$$\Rightarrow \frac{\nu_1}{\nu_2} = \frac{6.56 \times 10^{-5}}{4.10 \times 10^{-5}} = 1.6 : 1$$

Now the energy associated with electromagnetic radiation is given by  $E = h\nu$

$$\Rightarrow \frac{E_1}{E_2} = \frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} = 1.6 : 1$$

Hence the ratio of energies is same as that of frequencies.

**Illustration - 2** A 100 W power source emits green light at a wavelength  $\lambda = 5000 \text{ \AA}$ . How many photons per minute are emitted by the source ?

**SOLUTION :**

Energy given out by the source per sec = Power (P)

$$\Rightarrow \text{Energy given by source in } t \text{ sec} = P \times t$$

As  $\lambda = 5000 \text{ \AA}$ , the energy per photon of green light is

$$\text{given by : } h\nu = \frac{hc}{\lambda}$$

$\Rightarrow$  Number of photons ( $n$ ) emitted in time  $t$  sec is

$$\text{given by : } n = \frac{Pt}{(hc/\lambda)} = \frac{Pt\lambda}{hc}$$

Using  $P = 100 \text{ J/s}$ ,  $\lambda = 5000 \times 10^{-10} \text{ m}$  and  $t = 60 \text{ s}$

$\Rightarrow$  Number of photons ( $n$ ) :

$$= \frac{100(60) (5000 \times 10^{-10})}{(6.626 \times 10^{-34}) (3 \times 10^8)} = 1.5 \times 10^{22}$$

**Photoelectric Effect :**

It was observed by [Hertz](#) and [Lenard](#) around 1880 that when a clean metallic surface is irradiated by monochromatic light of proper frequency, electrons are emitted from it. This phenomenon of ejection of the electrons from metal surface was called as *Photoelectric Effect*.

- It was observed that if the frequency of incident radiation is below a certain minimum value (*threshold frequency*), no emission takes place however high the intensity of light may be.
- Another important feature observed was that the kinetic energy of the electrons emitted was independent of the intensity of the light. The kinetic energy of the electrons increase linearly with the frequency of incident light radiation. This was highly contrary to the laws of Physics at that time i.e. *the energy of the electrons should have been proportional to the intensity of the light, not to the frequency*.

*These features could not be properly explained on the basis of Maxwell's concept of light i.e. light as electromagnetic wave.*

In 1905, [Einstein](#) applied Planck's quantum theory of light to account for the extraordinary features of the photoelectric effect. *He introduced a new concept that light shows dual nature. In phenomenon like reflection, refraction and diffraction, it shows wave nature and in phenomenon like photoelectric effects, it shows particle nature.* According to the particle nature, the energy of the light is carried in discrete units whose magnitude is proportional to the frequency of the light wave. These units were called as *photons* (or *quanta*).

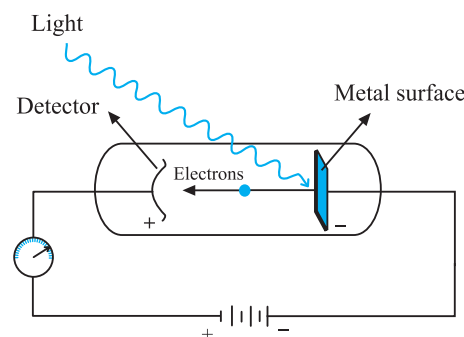
According to Einstein, when a quantum of light (photon) strikes a metal surface, it imparts its energy to the electrons in the metal. In order for an electron to escape from the surface of the metal, it must overcome the attractive force of the positive ions in the metal. So a part of the photon's energy is absorbed by the metal surface to release the electron, this is known as *work function* of the surface and is denoted by  $W_0$ . The remaining part of the energy of the photon goes into the kinetic energy of the electron emitted. If  $E_i$  is the energy of the photon,  $KE$  is the kinetic energy of the electron and  $W_0$  be the work function of the metal then we have ;

$$E_i = KE + W_0 \quad (\text{This is known as Einstein's photoelectric equation})$$

For each metal, there is a characteristic minimum frequency known as the *threshold frequency* ( $\nu_0$ ) below which the photoelectric effect does not occur. Electrons are emitted only after the frequency of light is equal to or above the threshold frequency. The threshold frequency is proportional to the work function of the metal. If  $\nu_0$  be the threshold frequency and  $\nu$  the frequency of incident light,  $E$  is energy of incident light, then we have :

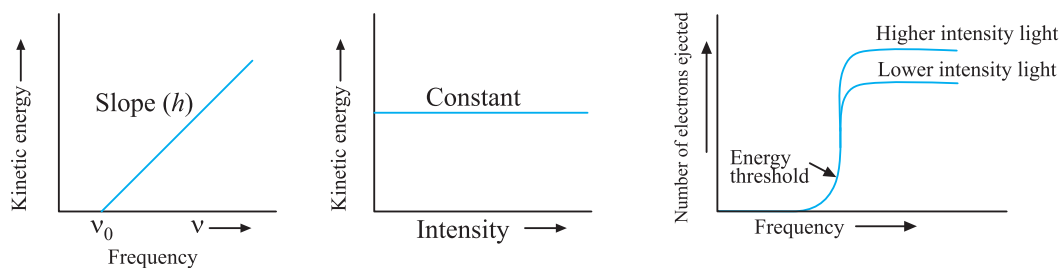
$$\begin{aligned} W_0 &= h \nu_0 & \text{and} & & E_i &= h \nu \\ \Rightarrow KE &= E_i - W_0 & \text{or} & & KE &= h \nu - h \nu_0 = h (\nu - \nu_0) \end{aligned}$$

Also, if  $m$  be the mass and  $v$  be the velocity of the electron ejected then  $KE = \frac{1}{2}mv^2 = h(\nu - \nu_0)$



#### Note :

- The Electromagnetic radiation (or wave) now emerges as an entity which shows dual nature i.e. sometimes as *Wave* and sometimes as *Particle* (quantum aspect).
- The energy of an individual photon depends only on its frequency and not on the intensity of the light beam. The intensity of a light beam is a measure of the number of photons in the beam and not of the energies of those photons. A low-intensity beam of high-energy photons might easily knock out electrons from a metal but a high intensity beam of low energy photons might not be able to knock out a single electron.



- Sometimes, it is convenient to calculate energy (in eV) of a photon in short form using :

$$E_p = \frac{hc}{\lambda} = \frac{12400}{\lambda(\text{in } \text{\AA})} \text{ eV} \equiv \frac{1240}{\lambda(\text{in nm})} \text{ eV}$$

#### Illustration - 3

Calculate the velocity of electron ejected from platinum surface when radiation of 200 nm falls on it.

Work function of platinum is 5 eV. ( $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ )

**SOLUTION :**

Using Einstein's photoelectric equation :

$$E_i = KE + W_0$$

where  $E_i$  : energy of incident radiation ;

KE : kinetic energy of ejected electron

 $W_0$  : work function of metal

$$E_i = \frac{1240}{200} \text{ eV} = 6.2 \text{ eV} ; \quad \text{and } W_0 = 5 \text{ eV}$$

$$\Rightarrow KE = E_i - W_0 = (6.2 - 5) \text{ eV} = 1.2 \text{ eV}$$

$$= 1.2 \times 1.6 \times 10^{-19} \text{ J} = 1.94 \times 10^{-19}$$

$$\text{Now, } KE = \frac{1}{2} mv^2 \Rightarrow v = \sqrt{\frac{2KE}{m}}$$

$$\Rightarrow v = \sqrt{\frac{2(1.94 \times 10^{-19})}{(9.1 \times 10^{-31})}} = 6.52 \times 10^5 \text{ m/s}$$

**Illustration - 4**

A photon of light with  $\lambda = 400 \text{ nm}$  falls on a metal surface. As a result, photoelectrons are ejected with a velocity of  $6.4 \times 10^5 \text{ m/s}$ . Find :

- (a) the kinetic energy of emitted photoelectrons, (b) the work function (in eV) of the metal surface.

**SOLUTION :**

(a) Kinetic energy of electron =  $\frac{1}{2} mv^2$

$$\Rightarrow KE = \frac{1}{2} (9.1 \times 10^{-31}) (6.4 \times 10^5)^2 = 1.86 \times 10^{-19} \text{ J}$$

$$= 1.16 \text{ eV}$$

(b) From Einstein's photoelectric equation :

$$E_i = KE + W_0 \Rightarrow W_0 = E_i - KE$$

$$\Rightarrow W_0 = \frac{1240}{400} - KE = 3.1 - 1.16 = 1.94 \text{ eV}$$

$$\Rightarrow W_0 = 1.94 \text{ eV}$$

**IN-CHAPTER EXERCISE - A**

- Suppose  $10^{-17} \text{ J}$  of light energy is needed by the interior of the human eye to see an object. How many photons of green light ( $\lambda = 550 \text{ nm}$ ) are needed to generate this minimum amount of energy ?
- A photon of  $300 \text{ nm}$  is absorbed by a gas and then re-emits two photons. One re-emitted photon has wavelength  $400 \text{ nm}$ . Calculate energy of other photon re-emitted out.
- The energy required to stop the ejection of electrons from Cu plate is  $0.24 \text{ eV}$ , when the radiation of wavelength  $\lambda = 300 \text{ nm}$  strikes the plate. Calculate the work function of Cu.
- The minimum energy required to overcome the attractive forces between electron and the surface of Ag metal is  $7.52 \times 10^{-19} \text{ J}$ . What will be maximum KE of an electron ejected out from Ag which is being exposed to UV radiations of  $\lambda = 360 \times 10^{-10} \text{ m}$  ?
- An oil drop has  $6.39 \times 10^{-19} \text{ C}$  charge. How many electrons does this oil drop have ?

Choose the correct option for each of the following.

- The ratio of  $e/m$ , i.e., specific charge for a cathode ray :
  - has the smallest value when the discharge tube is filled with  $H_2$
  - is constant
  - varies with the atomic number of gas in the discharge tube
  - varies with the atomic number of an element forming the cathode
- Consider a  $20 \text{ W}$  light source that emits monochromatic light of wavelength  $600 \text{ nm}$ . The number of photons ejected per second in form of Avogadro's constant  $N_{AV}$  is approximately :
  - $N_{AV}$
  - $10^{-2} N_{AV}$
  - $10^{-4} N_{AV}$
  - $10^{-6} N_{AV}$

8. Rutherford's experiment, which established the nuclear model of the atom, used a beam of :  
 (A)  $\beta$ -particles, which impinged on a metal foil and got absorbed  
 (B)  $\gamma$ -rays, which impinged on a metal foil and ejected electrons  
 (C) Helium atoms, which impinged on a metal foil and got scattered  
 (D) Helium nuclei, which impinged on a metal foil and got scattered.
9. Of the following, radiation with maximum wavelength is :  
 (A) UV (B) Radio wave (C) X-rays (D) IR
10. When a certain metal was irradiated with light of frequency  $3.2 \times 10^{16}$  Hz, photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency  $2.0 \times 10^{16}$  Hz. Hence threshold frequency is :  
 (A)  $0.8 \times 10^{15}$  Hz (B)  $8.0 \times 10^{15}$  Hz (C)  $0.8 \times 10^{14}$  Hz (D)  $6.4 \times 10^{16}$  Hz
11. How many photons are emitted per second by a 10 mW laser source operating at 626 nm ?  
 (A)  $1.6 \times 10^{16}$  (B)  $1.6 \times 10^{18}$  (C)  $3.2 \times 10^{16}$  (D) None of these
12. If the frequency of light in a photoelectric experiment is doubled, the stopping potential will :  
 (A) be doubled (B) be halved  
 (C) become more than double (D) become less than double

## ATOMIC SPECTRA OF HYDROGEN AND BOHR'S MODEL

## SECTION - 3

It is observed that the atoms of hydrogen in gas discharge tube emit radiations whose spectrum shows line characteristics (line spectra). The line spectra of hydrogen lies in three regions of Electromagnetic Spectrum: *Infra-red*, *Visible* and *UV* region. In all there are five sets of discrete lines.

The set of lines in the *Visible* region are known as *Balmer Series*, those in *Ultra-Violet* as *Lyman series* and there are three sets of lines in *Infra-red* region : *Paschen*, *Brackett* and *Pfund series*. Balmer and Rydberg gave an empirical relation to define the wavelength of the lines in each series in terms of a parameter called as *Wave Number* denoted by  $\bar{\nu}$ . The wave number is defined as reciprocal of the wavelength i.e.,  $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = RZ^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$

where  $n$  and  $m$  are whole numbers;  $\lambda$  : wavelength of spectral line ;  $\bar{\nu}$  : wave number of spectral line  
 $R$  : Rydberg constant. The values of  $n$  and  $m$  for different spectral lines for each series are listed below.

Region	Spectral line	$n$	$m$
UV	Lyman Series	1	2, 3, 4, ...
Visible	Balmer Series	2	3, 4, 5, ...
Infra-red	Paschen Series	3	4, 5, 6, ...
Infra-red	Brackett Series	4	5, 6, ...
Infra-red	Pfund Series	5	6, 7, ...
	Humphry Series	6	8, 7, 8 ...



**In Hydrogen atom spectra :**

- Intermediate frequencies were emitted i.e. only specific spectral lines are there in the spectrum (Planck's quantum theory).
- Lines observed were characteristic of Hydrogen atom only.

These observations led **Bohr** to conclude that electrons in an atom are not randomly distributed, but were arranged in definite energy states. The energy of each state (or level) was fixed or quantised (from characteristic nature of H-atom spectra). The complete theory developed by him is organised in his postulates.

**Bohr's Postulates**

Bohr's theory was based on the application of Planck's Quantum theory on the atomic spectra of Hydrogen atom. The fundamental postulates of his theory are discussed below :

- The electron in an atom has only certain definite stationary states of motion allowed to it, called as *energy levels*. Each energy level has a definite energy associated with it. In each of these energy levels, electrons move in circular orbit around the positive nucleus. The necessary centripetal force is provided by the electrostatic attraction of the protons in the nucleus. As one moves away from the nucleus, the energy of the states increases.
- These states of allowed electronic motion are those in which the angular momentum of an electron is an integral multiple of  $\frac{h}{2\pi}$  or one can say that the angular momentum of an electron is quantised.

$$\Rightarrow \text{Angular momentum} = mvr = n \left( \frac{h}{2\pi} \right) \quad \begin{aligned} \text{Angular momentum} &= \text{moment of Inertia} \times \text{angular velocity} \\ &= mr^2 \times \frac{v}{r} = mvr \end{aligned}$$

where  $m$  is the mass of the electron,  $v$  is the velocity of the electron,  $r$  is the radius of the orbit,  $h$  is Planck's constant and  $n$  is a positive integer.

- When an atom is in one of these states, it does not radiate any energy but whenever there is a transition from one state to other, energy is emitted or absorbed depending upon the nature of transition.

When an electron jumps from higher energy state to the lower energy state, it emits radiations in form of photons or quanta. However, when an electron moves from lower energy state to a higher state, energy is absorbed, again in form of photons.

The energy of a photon emitted or absorbed is given by using Planck's relation ( $E = h\nu$ ). If  $E_1$  be the energy of any lower energy state and  $E_2$  be the energy of any higher energy state, then the energy of the photon (emitted or absorbed) is given as  $\Delta E$  (i.e., the difference in the energies of two states) :  $\Delta E = E_2 - E_1 = h\nu = h \frac{c}{\lambda}$

where  $h$  : Planck's constant and  $\nu$  : frequency of radiation emitted or absorbed.

**Additional Information :**

*Coulomb's Law of Electrostatic force of attraction or repulsion ( $F$ )* between two charges  $q_1$  and  $q_2$  separated by a distance

' $r$ ' is given by :  $\text{Force (F)} = \frac{K |q_1| |q_2|}{r^2}$  where  $K = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$

Note that charge on any particle can only be an integral multiple of charge on an electron ( $e$ ).

Electrostatic Potential energy (E.P.E.) of a system of two charges separated by a distance ' $r$ ' is given by :

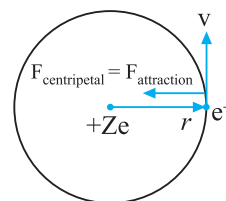
$$\text{E.P.E.} = \frac{Kq_1q_2}{r}$$

**Note :** E.P.E. is +ve when charges are like and -ve when charges are opposite.

Electrostatic force ( $F$ ) is repulsive when both  $q_1$  and  $q_2$  are of same sign (i.e. either both are positive or both are negative) and is attractive when  $q_1$  and  $q_2$  are of different signs.

### Bohr Model :

Consider a species of atomic number ( $Z$ ) containing single electron revolving around its nucleus at a distance of ' $r$ ' as shown in the figure.



**Note :** Atomic number  $\equiv$  Number of protons on the nucleus =  $Z$

$\Rightarrow$  Charge on the nucleus =  $+Ze$  [As charge on each proton is  $+e$  and neutrons don't have any charge]

Electrostatic force of attraction ( $F$ ) between the nucleus of charge  $+Ze$  and electron ( $-e$ ) is given by :

$$F = \frac{K|Ze||-e|}{r^2} = \frac{KZe^2}{r^2} \quad \dots (i)$$

The centrifugal forces acting on the electron is  $\frac{m_e v^2}{r}$   $\dots (ii)$

[Assuming uniform circular motion]

This centrifugal force must be provided by the electrostatic force of attraction ( $F$ ).

$\Rightarrow$  From (i) and (ii), we have :

$$\frac{KZe^2}{r^2} = \frac{m_e v^2}{r} \quad \dots (iii)$$

Also, according to Bohr's postulate of quantization of angular momentum, we have :

$$\text{Angular momentum of electron about the nucleus} = m_e v r = \frac{nh}{2\pi} \quad \dots (iv)$$

where ' $n$ ' is a positive integer

$$(n = 1, 2, 3, \dots, \infty)$$

Solve (iii) and (iv) to get :

$$v = \frac{2\pi KZe^2}{nh} \quad \text{and} \quad r = \frac{n^2 h^2}{4\pi^2 K m_e e^2 Z}$$

Put  $K = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$ ,  $e = 1.6 \times 10^{-19} \text{ C}$  and  $h = 6.626 \times 10^{-34} \text{ Js}$  in the above expressions to get :

$$\text{Velocity of an electron in } n\text{th Bohr orbit} \equiv v_n = 2.18 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$$

$$\text{and Radius of the } n\text{th Bohr orbit} \equiv r_n = 0.529 \times 10^{-10} \frac{n^2}{Z} \text{ m} \equiv 0.529 \frac{n^2}{Z} \text{ \AA} \equiv 52.9 \frac{n^2}{Z} \text{ pm} \quad [1 \text{ pm} = 10^{-12} \text{ m}]$$

Now, the Total Energy of the electron moving in  $n$ th orbit  $\equiv K.E._n + E.P.E._n$

$$\text{T.E.}_n = \frac{1}{2} m v_n^2 + \frac{K(Ze)(-e)}{r} \quad \left[ \because E.P.E. \equiv \frac{Kq_1q_2}{r} \right]$$

$$\Rightarrow T.E_n = \frac{1}{2} \left( \frac{KZe^2}{r_n} \right) + \frac{K(Ze)(-e)}{r_n} \quad [\text{Using (iii)}]$$

$$\Rightarrow E_n \equiv T.E_n = \frac{-KZe^2}{2r_n}$$

It can be shown from the above expressions that :

$$K.E._n = \frac{1}{2} \frac{KZe^2}{r_n}, \quad P.E._n = \frac{-KZe^2}{r_n} \quad \text{and} \quad E_n = \frac{-KZe^2}{2r_n}$$

or  $K.E._n = -E_n$  and  $E.P.E._n = 2E_n$

Using the value of  $r_n$  in the expression of  $E_n$ , we get :

$$E_n = \frac{-2\pi^2 K^2 m_e e^4 Z^2}{n^2 h^2}$$

$$E_n = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom} = -13.6 \frac{Z^2}{n^2} \text{ eV/atom} \quad \left[ \because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} \right]$$

$$= -2.18 \times 10^{-18} \frac{Z^2}{n^2} \times 6.02 \times 10^{23} \text{ J/mole} = -1312 \frac{Z^2}{n^2} \text{ kJ/mole}$$

**Note:** ➤ Bohr's Model is applicable only to one-electron atoms like :  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  apart from H-atom.

### Illustration - 5

Determine the frequency of revolution of the electron in 2nd Bohr's orbit in hydrogen atom.

#### SOLUTION :

The frequency of revolution of electron is given by :

$$\text{Frequency} = \frac{1}{\text{time period}}$$

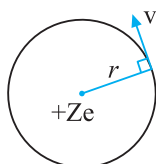
Time period

$$= \frac{\text{Total distance covered in 1 revolution}}{\text{velocity}} = \frac{2\pi r}{v}$$

$$\text{Hence frequency} = \frac{v}{2\pi r}$$

Calculate velocity ( $v_2$ ) and radius ( $r_2$ ) for electron in 2nd Bohr orbit in H-atom ( $Z = 1$ )

$Z = 1$  for H-atom.



$$\text{Using } r_n = 0.529 \frac{n^2}{Z} \text{ \AA}$$

$$r_2 = 0.529 \times 10^{-10} \frac{(2)^2}{1} \text{ m} = 1.12 \times 10^{-10} \text{ m}$$

$$v_n = 2.18 \times 10^6 (1/n) \text{ m/s}$$

$$v_2 = 2.18 \times 10^6 (1/2) = 1.09 \times 10^6 \text{ m/s}$$

$$\text{Hence frequency} = \frac{v_2}{2\pi r_2} = \frac{1.09 \times 10^6}{2(\pi)(1.12 \times 10^{-10})}$$

$$v = 8.18 \times 10^{14} \text{ Hz.}$$

**Note:** Frequency of revolution ( $f$ ) =  $1/T$  where  $T = \frac{2\pi r}{v} \propto \frac{n^3}{Z^2}$   $\left[ \because r \propto \frac{n^2}{Z} \text{ and } v \propto \frac{Z}{n} \right]$

$$\Rightarrow f \propto \frac{Z^2}{n^3}$$

**What does the negative electron energy ( $E_n$ ) means ?**

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits. What do this negative sign convey ? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. An electron in an atom is because of attractive force due to protons in the nucleus. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting  $n$  equal to infinity in the equation so that  $E_\infty = 0$ . As electron gets closer to the nucleus,  $E_n$  becomes larger in absolute value and more and more negative. The most negative energy value is given by  $n = 1$  which corresponds to the most stable orbit.

When an electron jumps from an outer orbit (higher energy)  $n_2$  to an inner orbit (lower energy)  $n_1$ , then the energy emitted in form of radiation is given by :

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 K^2 m e^4 Z^2}{h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \Rightarrow \Delta E = 2.18 \times 10^{-18} \times Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Also,  $\Delta E = 13.6 \times Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV/atom}$

As we know that :  $E = h\nu$  ;  $\bar{\nu} = \frac{1}{\lambda}$   $\Rightarrow \bar{\nu} = \frac{\Delta E}{hc} = \frac{2\pi^2 K^2 m e^4 Z^2}{c h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

The above equation can be represented as :  $\bar{\nu} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$  where  $R = \frac{2\pi^2 K^2 m e^4}{c h^3}$

$R$  is known as Rydberg constant. Its value to be used is  $= 109677 \text{ cm}^{-1} = 10967700 \text{ m}^{-1}$

**Note :** (i) The value of  $\frac{1}{R} \approx 911.5 \text{ \AA}$  is sometimes useful.

(ii) This relation exactly matches with the empirical relation given by **Balmer** and **Rydberg** to account for the spectral lines in H-atom spectra. In fact the value of Rydberg constant in the empirical relation is approximately the same as calculated from the above relation (**Bohr's Theory**). This was the main success of Bohr's Theory i.e. to account for the experimental observations by postulating a theory.

(iii) The maximum number of lines that can be emitted when an electron in an excited state  $n = n_2$  de-excites to a state  $n = n_1$  ( $n_2 > n_1$ ) is given by :  $\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$

**Illustration - 6** Determine the maximum number of lines that can be emitted when an electron in H atom in  $n = 6$  state drops to the ground state. Also find the transitions corresponding to the lines emitted.

**SOLUTION :**

The maximum number of lines can be calculated by using the above formula with  $n_2 = 6$  and  $n_1 = 1$  are 15.

The distinct transitions corresponding to these lines are:

6  $\rightarrow$  1  
6  $\rightarrow$  2, 2  $\rightarrow$  1  
6  $\rightarrow$  3, 3  $\rightarrow$  2, 3  $\rightarrow$  1  
6  $\rightarrow$  4, 4  $\rightarrow$  3, 4  $\rightarrow$  2, 4  $\rightarrow$  1  
6  $\rightarrow$  5, 5  $\rightarrow$  4, 5  $\rightarrow$  3, 5  $\rightarrow$  2, 5  $\rightarrow$  1

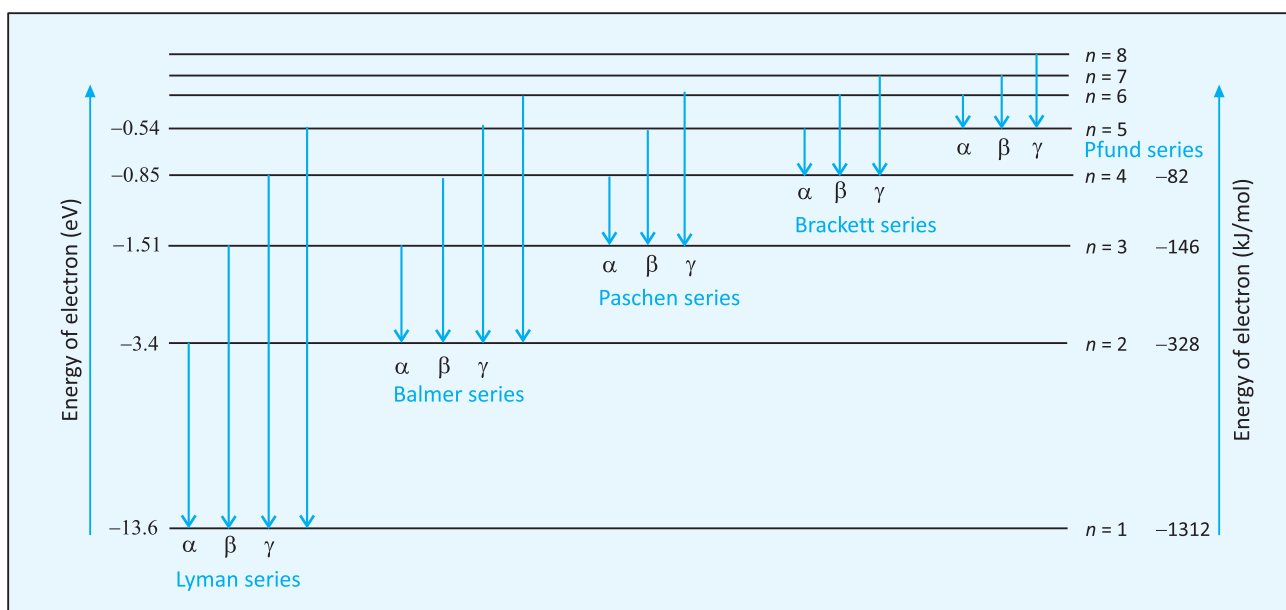
**Note :** Each line (in emission spectra) corresponds to a particular photon emitted. The photon with shortest wavelength is corresponding to the largest energy difference (6  $\rightarrow$  1) and with longest wave length is corresponding to minimum energy difference (6  $\rightarrow$  5).

## ENERGY LEVELS OF HYDROGEN ATOM

## SECTION - 4

The spectrum of H-atom studied by *Lyman*, *Balmer*, *Paschen*, *Brackett* and *Pfund* can now be explained on the basis of Bohr's Model.

It is now clear that when an electron jumps from a higher energy state to a lower energy state, the radiation is emitted in form of photons. The radiation emitted in such a transition corresponds to the spectral line in the atomic spectra of H-atom.



Spectral Lines and Energy Levels of Hydrogen atom

## Lyman Series

When an electron jumps from any of the higher states to the ground state or 1st state ( $n = 1$ ), the series of spectral lines emitted lies in *ultra-violet region* and are called as *Lyman Series*. The wavelength (or wave number) of any line of the series

can be given by using the relation :  $\bar{\nu} = R Z^2 \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right)$   $n_2 = 2, 3, 4, 5, \dots$

**Note:** For H-atom,  $Z = 1$  ;  $\text{He}^+$  ion,  $Z = 2$  and  $\text{Li}^{2+}$ ,  $Z = 3$

## Balmer Series

When an electron jumps from any of the higher states to the state with  $n = 2$  (IInd state), the series of spectral lines emitted lies in *visible region* and are called as *Balmer Series*. The wave number of any spectral line can be given by using the

relation :  $\bar{\nu} = R Z^2 \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)$   $n_2 = 3, 4, 5, \dots$

## Paschen Series

When an electron jumps from any of the higher states to the state with  $n = 3$  (IIIrd state), the series of spectral lines emitted lies in *near infra-red region* and are called as *Paschen Series*. The wave number of any spectral line can be given by using

the relation :  $\bar{\nu} = R Z^2 \left( \frac{1}{3^2} - \frac{1}{n_2^2} \right)$   $n_2 = 4, 5, 6, \dots$

**Brackett Series**

When an electron jumps from any of the higher states to the state with  $n = 4$  (IVth state), the series of spectral lines emitted lies in *far infra-red region* and called as *Brackett Series*. The wave number of any spectral line can be given by using the

$$\text{relation : } \bar{\nu} = R Z^2 \left( \frac{1}{4^2} - \frac{1}{n_2^2} \right) \quad n_2 = 5, 6, 7, \dots$$

**Pfund Series**

When an electron jumps from any of the higher states to the state with  $n = 5$  (Vth state), the series of spectral lines emitted lies in *far infra-red region* and are called as *Pfund Series*. The wave number of any spectral line can be given by using the

$$\text{relation : } \bar{\nu} = R Z^2 \left( \frac{1}{5^2} - \frac{1}{n_2^2} \right) \quad n_2 = 6, 7, \dots$$

Note that Lyman series in UV region, Balmer series in visible region and Paschen, Brackett & Pfund series in Infra-red region are only for H-atom ( $Z = 1$ ).

**Note :** In a particular series, **First**  $[(n_1 + 1) \rightarrow n_1]$ , **second**  $[(n_1 + 2) \rightarrow n_1]$ , **third**  $[(n_1 + 3) \rightarrow n_1]$  . . . lines are called as  $\alpha$ ,  $\beta$ ,  $\gamma$ , . . . lines respectively. For example  $\beta$ -line in Balmer series corresponds to  $(2 + 2) \rightarrow 2$  i.e.,  $4 \rightarrow 2$ . In Lyman series :  $\alpha$ -line  $\equiv 2 \rightarrow 1$  ;  $\beta$ -line  $\equiv 3 \rightarrow 1$  ;  $\gamma$ -line  $\equiv 4 \rightarrow 1$ .

The energy required to remove the electron from the outermost orbit of the atom in gaseous phase is called as *Ionisation energy*. Here, since we are considering only one electron species, Ionisation energy ( $IE$ ) =  $-E_1 = +13.6 Z^2 \text{ eV}$ .

**Illustration - 7**

The Lyman series of Hydrogen spectrum can be represented by the equation :

$$\nu = 3.28 \times 10^{15} \left[ \frac{1}{1^2} - \frac{1}{n^2} \right] \text{ s}^{-1}. \text{ Calculate the maximum and minimum frequency in this series.}$$

**SOLUTION :**

Lyman frequency will be maximum corresponding to maximum energy transition. i.e.  $1 \rightarrow \infty$

$$\Rightarrow \nu_{\max} = 3.28 \times 10^{15} \left[ \frac{1}{1^2} - \frac{1}{\infty^2} \right] \text{ s}^{-1} = 3.28 \times 10^{15} \text{ s}^{-1}$$

Note that corresponding wavelength will be shortest wavelength.

And Lyman frequency will be minimum corresponding to minimum energy transition. i.e.  $1 \rightarrow 2$

$$\Rightarrow \nu_{\min} = 3.28 \times 10^{15} \left[ \frac{1}{1^2} - \frac{1}{2^2} \right] \text{ s}^{-1} = 2.46 \times 10^{15} \text{ s}^{-1}$$

Note that corresponding wavelength will be longest wavelength.

**Illustration - 8**

The wavelength of second line (also called as  $\beta$ -line) in Balmer series of hydrogen atom is :

- (A) 656.28 Å      (B) 4872 Å      (C) 6562.8 Å      (D) 486.2 Å

**SOLUTION :**

The transition responsible for second Balmer ( $\beta$ -line) line is  $4 \rightarrow 2$ . In H-atom,  $n_1 = 2$  for Balmer series.

$$\Rightarrow \Delta E = 13.6 (1)^2 \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 2.55 \text{ eV}$$

$$\text{Now } \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.55 \times 1.6 \times 10^{-19}}$$

$$\Rightarrow \lambda = 4.872 \times 10^{-7} \text{ m} = 4872 \text{ Å}$$

Hence correct option is (B).



**Illustration - 9** A spectral line in the spectrum of H-atom has a wave number of  $15222.22 \text{ cm}^{-1}$ . The transition responsible for this radiation is : (Rydberg constant  $R = 109677 \text{ cm}^{-1}$ ).

- (A)  $2 \rightarrow 1$       (B)  $4 \rightarrow 2$       (C)  $3 \rightarrow 2$       (D)  $2 \rightarrow 3$

**SOLUTION :**

$$\lambda = 1/\bar{\nu} = 1/15222.22 = 6.569 \times 10^{-5} \text{ cm} = 6569 \text{ \AA}$$

Clearly, it lies in Visible region i.e, in Balmer series.

Hence  $n_1 = 2$

Using the relation for wave number for H-atom:

$$\bar{\nu} = 1/\lambda = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$15222.22 = 109677 \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow n_2 = 3$$

$\Rightarrow$  the required transition is  $3 \rightarrow 2$

Hence (C) is correct.

**Note :** (D) is wrong, since  $2 \rightarrow 3$  will absorb radiation.

### Drawbacks of Bohr model :

Bohr's model was successful in explaining the spectra and hence the structure of Hydrogen atom; still many questions were not answered.

- His postulates combined two different concepts : one from classical physics and second from modern theory of quantization.
- It could not explain the spectrum of atoms or ions having two or more electrons. It accounted only for the spectra of H-atom,  $\text{He}^+$  ion and  $\text{Li}^{++}$  ion.
- There was no justification for the quantization of angular momentum of an electron, though this was a correct assumption.
- His model could not provide a satisfactory picture of Chemical Bond.
- It also failed to account for the brightness of the spectral lines, splitting spectral lines in electric field (Stark Effect) and in magnetic field (Zeeman Effect).

**Illustration - 10** Calculate the wavelength of light radiation that would be emitted, when an electron in the fourth Bohr's orbit of  $\text{He}^+$  ion falls to the second Bohr's orbit. To what transition does this light radiation correspond in the H-atom ?

**SOLUTION :**

First calculate the energy difference ( $\Delta E$ ) between 4th and 2nd Bohr orbit using :

$$\Delta E_{(4 \rightarrow 2)} = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV}$$

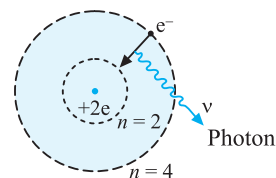
Substituting  $n_1 = 2$  and  $n_2 = 4$ ,  $Z = 2$  we get ;

$$\Delta E = 10.2 \text{ eV}$$

This energy difference (energy lost by the electron) will be equal to the energy of the emitted photon.

$$\text{Using : } \lambda = \frac{12400}{E_{\text{photon}} (\text{eV})} \text{ \AA} = \frac{12400}{10.2} \text{ \AA} = 1215.7 \text{ \AA}$$

Note : The emitted radiation is in UV region which implies that, in H-atom this transition would lie in Lyman Series ( $n_1 = 1$ ).



Hence our aim is now to find the transition :  $n_2 \rightarrow 1$

$$\text{Use : } \Delta E_{(n_2 \rightarrow 1)} = 13.6 \times 1^2 \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right) \text{ eV} \Rightarrow 10.2 = 13.6 \left( 1 - \frac{1}{n_2^2} \right) \text{ eV} \Rightarrow n_2 = 2$$

Hence the corresponding transition in H-atom is  $2 \rightarrow 1$

**Note :** This concept can be applied only for H-atom.

**Alternate Approach :**

$$\text{As discussed above : } \Delta E_{(4 \rightarrow 2)} \text{ (in He}^+) = \frac{hc}{\lambda_{\text{Photon}}} = 13.6 \times 2^2 \times \left( \frac{1}{2^2} - \frac{1}{4^2} \right) \text{ eV} \quad \dots(i)$$

$$\Delta E_{(n_2 \rightarrow n_1)} \text{ (in H)} = \frac{hc}{\lambda_{\text{Photon}}} = 13.6 \times 1^2 \times \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV} \quad \dots(ii)$$

Try to convert equation (ii) in the form given in equation (i) and compare it with equation (i) as below :

$$\Rightarrow \Delta E_{(4 \rightarrow 2)} \text{ (in He}^+) = \frac{hc}{\lambda_{\text{Photon}}} = 13.6 \times 1^2 \times \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \text{ eV} \quad [2^2 \text{ shifted inside}]$$

On comparing the above equation with equation (i), we get :  $n_1 = 1$  and  $n_2 = 2$

**Note :** This concept can be applied for any H-like species.

**Illustration - 11** Find the wavelength of radiation required to excite the electron in ground level of  $\text{Li}^{++}$  ( $Z = 3$ ) to third energy level. Also find the ionisation energy of  $\text{Li}^{++}$ . ( $R = 109,677 \text{ cm}^{-1}$ )

**SOLUTION :**

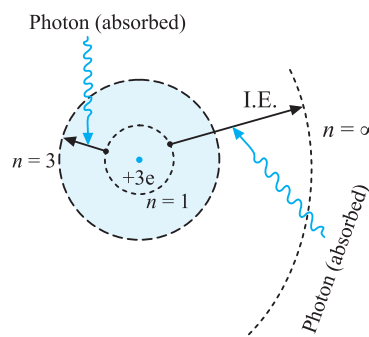
Ground level :  $n = 1$

$$\text{Use : } \frac{1}{\lambda} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Putting the values :  $n_1 = 1, n_2 = 3, Z = 3$

$$\text{We get : } \frac{1}{\lambda} = 109677 \times 3^2 \times \left( \frac{1}{1^2} - \frac{1}{3^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} = 877416 \text{ cm}^{-1} \Rightarrow \lambda = \frac{1}{\nu} = 113.97 \text{ \AA}$$



Ionisation energy is the energy required to remove the electron from ground state to infinity i.e. corresponding transition responsible is  $1 \rightarrow \infty$ .

$$\text{i.e. } \Delta E_{(1 \rightarrow \infty)} = 13.6 \times 3^2 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) \text{ eV}$$

$$\text{Ionisation energy} = \Delta E_{(1 \rightarrow \infty)} = 122.4 \text{ eV} = 1.95 \times 10^{-17} \text{ J} \quad [\because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}]$$

**Note :** Ionisation Energy (IE)  $= -E_1 = +13.6 Z^2 \text{ eV}$

**Illustration - 12** Find the energy released (in ergs) when 2.0 gm atom of Hydrogen atoms undergo transition giving spectral line of lowest energy in visible region of its atomic spectra.

## SOLUTION :

For H-atom, the spectral lines in visible region correspond to Balmer Lines ( $n_1 = 2$ ). Now for lowest energy photon, the required transition will be from  $3 \rightarrow 2$ .

Using the relation for  $\Delta E$  :

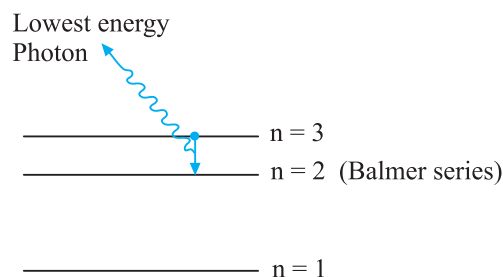
$$\Delta E = 2.18 \times 10^{-18} (1)^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \text{ J/atom}$$

$$= 3.03 \times 10^{-19} \text{ J}$$

Now for 2.0 gm-atoms, the energy released will be

$$E = (2 \times 6.023 \times 10^{23}) \times 3.03 \times 10^{-19} \text{ J}$$

$$= 3.65 \times 10^5 \text{ J} \equiv 3.65 \times 10^{12} \text{ [1J} \equiv 10^7 \text{ ergs]}$$



## IN-CHAPTER EXERCISE - B

- Calculate the longest wavelength, which can remove the electron from 2nd Bohr orbit to infinity in  $\text{Li}^{2+}$  ion. Given  $E_1$  for H-atom = 13.6 eV.
- What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$  spectrum ?
- The wavelength of a certain line in the H-atom spectra is observed to be 434.1 nm for hydrogen atom. To what value of  $n_2$  does this line correspond ? Given : Rydberg constant =  $109677 \text{ cm}^{-1}$ .
- When an electron makes a transition from  $n = 3$  to  $n = 1$  in a Hydrogen atom, find the change in potential energy of the atom.
- Given ionisation potential of H atom is 13.6 eV. Find the frequency and wavelength of  $H_\beta$  line of Balmer series.
- Calculate :
  - The series limit for Balmer series of H spectrum.
  - Ionisation energy of H atom.
  - Wavelength of the photon that would ionize this H atom.
- The first IE of potassium is  $100 \text{ kcal mole}^{-1}$ . Calculate the lowest possible frequency of light that can ionise a potassium atom.

Choose the correct alternative. Only One choice is Correct. However, questions marked with '\*' may have More than One correct option :

- The wavelength of a spectral line for an electronic transition is inversely related to :
  - the number of orbit undergoing the transition
  - the square of nuclear charge of an atom
  - the difference in energy levels involved in the transition
  - the velocity of the electron undergoing the transition
- In the hydrogen atom, the transition energy will be maximum for
 

(A) $n_5 \rightarrow n_4$	(B) $n_4 \rightarrow n_3$	(C) $n_3 \rightarrow n_2$	(D) will be the same in all transitions
---------------------------	---------------------------	---------------------------	---
- If the radius of the first Bohr orbit of the H atom is  $r$  then for the  $\text{Li}^{2+}$  ion it will be
 

(A) $3r$	(B) $9r$	(C) $r/3$	(D) $r/9$
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11. The wavelength of certain line in H-atom spectra is observed to be  $4341 \text{ \AA}$ . ( $R_H = 109677 \text{ cm}^{-1}$ ). The value of quantum number of higher state is :  
(A) 3 (B) 4 (C) 5 (D) Data insufficient
12. A certain transition in H-spectrum from an excited state to ground state in one or more steps gives rise to a total of ten lines. How many of these belong to visible spectrum ?  
(A) 3 (B) 4 (C) 5 (D) 6
13. According to Bohr model, angular momentum of an electron in the 3rd orbit is :  
(A)  $\frac{3h}{\pi}$  (B)  $\frac{1.5h}{\pi}$  (C)  $\frac{3\pi}{h}$  (D)  $\frac{9h}{\pi}$
14. An electron in H-atom is moving with a kinetic energy of  $5.45 \times 10^{-19} \text{ J}$ . What will be energy level for this electron ?  
(A) 1 (B) 2 (C) 3 (D) None of these
15. An electron jumps from 6th energy level to 3rd energy level in H-atom, how many lines belong to visible region ?  
(A) 1 (B) 2 (C) 3 (D) Zero
- \*16. Which of the following is(are) proportional to the energy of electromagnetic radiation ?  
(A) Frequency (B) Wave number (C) Wavelength (D) Number of photons
17. Which of the following best describes the emission spectrum of atomic hydrogen ?  
(A) A discrete series of lines of equal intensity and equally spaced with respect to wavelength  
(B) A series of only four lines  
(C) A continuous emission of radiation of all frequencies  
(D) Several discrete series of lines with both intensity and spacing between lines decreasing as the wave number increases with each series
- \*18. According to Bohr's theory :  
(A) when the atom gets the required energy from the outside, electrons jumps from lower orbits to higher orbits and remain there  
(B) when the atom gets the required energy from outside, electrons jumps from lower orbits to higher orbits and remain there for very short intervals of time and return back to the lower orbit, radiating energy  
(C) angular momentum of the electron is proportional to  $n$   
(D) angular momentum of the electron is independent of  $n$
19. If uncertainty in position of electron is zero, the uncertainty in its momentum would be :  
(A) zero (B)  $h/2\pi$  (C)  $h/4\pi$  (D) infinity
20. If  $E_1$ ,  $E_2$  and  $E_3$  represent respectively the kinetic energies of an electron, an alpha particle and a proton each having same de Broglie wavelength then :  
(A)  $E_1 > E_3 > E_2$  (B)  $E_2 > E_3 > E_1$  (C)  $E_1 < E_3 < E_2$  (D)  $E_1 = E_2 = E_3$
- \*21. Which of the following parameters are not same for all hydrogen like atoms and ions in their ground state ?  
(A) Radius of orbit (B) Speed of electron  
(C) Energy of the atom (D) Orbital angular momentum of electron
- \*22. Given ionisation potential of H atom is  $13.6 \text{ eV}$ . The frequency of  $H_\beta$  line of Lyman series is :  
(A)  $2.90 \times 10^{15} \text{ Hz}$  (B)  $3.07 \times 10^{15} \text{ Hz}$   
(C)  $1.02 \times 10^7 \text{ Hz}$  (D)  $9.7 \times 10^6 \text{ Hz}$

23. In which of the following system will the radius of the first orbit ( $n = 1$ ) be minimum ?  
(A) hydrogen atom (B) deuterium atom  
(C) singly ionized helium (D) doubly ionized lithium
24. In which of the following system will the wavelength corresponding to  $n = 2$  to  $n = 1$  be minimum ?  
(A) hydrogen atom (B) deuterium atom  
(C) singly ionized helium (D) doubly ionized lithium
25. The energy of an atom (or ion) in its ground state is 54.4 eV. It may be :  
(A) hydrogen (B) deuterium (C)  $\text{He}^+$  (D)  $\text{Li}^{++}$
26. A hydrogen atom in ground state absorbs 10.2 eV of energy. The orbital angular momentum of the electron is increased by:  
(A)  $1.05 \times 10^{-34} \text{ J-s}$  (B)  $2.11 \times 10^{-34} \text{ J-s}$  (C)  $3.16 \times 10^{-34} \text{ J-s}$  (D)  $4.22 \times 10^{-34} \text{ J-s}$
27. A photon was absorbed by a hydrogen atom in its ground state and the electron was promoted to the fifth orbit. When the excited atom returned to its ground state, visible and other quanta were emitted. Other quanta are :  
(A)  $2 \rightarrow 1$  (B)  $5 \rightarrow 2$  (C)  $3 \rightarrow 1$  (D)  $4 \rightarrow 1$
28. Of the following, radiation with maximum wavelength is :  
(A) UV (B) Radio wave (C) X-ray (D) IR
29. Zeeman effect explain splitting of lines in :  
(A) Magnetic field (B) Electron field (C) Both (D) None of these

## WAVE NATURE OF PARTICLES

## SECTION - 5

We have studied that light shows dual nature i.e. wave nature (*Electromagnetic Radiation*) and particle nature (*photons*). In the following article we will see that not only light but *matter also shows dual nature*.

In 1923, [de Broglie](#) suggested that, since light is dualistic in nature: behaving in some aspects as waves and in others like particles, the same might be true of matter. According to him, every form of matter (electron or proton or any other particle) behaves like waves in some circumstances. These were called as *matter waves* or *de Broglie waves*. de Broglie postulated that a particle of mass  $m$  moving with a velocity  $v$  should have a wavelength  $\lambda$  given by :

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad (p = \text{linear momentum} = mv)$$

Now we can think of a model of atom where moving electrons (obviously around the nucleus) should behave like waves. The wave hypothesis of de Broglie was later developed by [Heisenberg](#), Schrödinger, [Fermi](#) and many others in modern atomic theory and is known as *wave mechanics* or *quantum mechanics*.

In new theory, electrons in an atom are visualised as diffused clouds surrounding the nucleus. The idea that the electrons in an atom move in definite orbits (*Bohr's model*) is now abandoned. The new theory assigns definite energy states to an atom but discards a definite path for movement of an electron.

Due to wave nature of electron in an atom, it is now highly impossible to ascertain the exact whereabouts of an electron. This idea is defined by **Heisenberg's Uncertainty Principle** as :

*“ It is impossible to specify at any given instant, both the momentum and the position of a sub-atomic particle like electron.”*

Whenever there is an attempt to specify the position of electron precisely, an uncertainty is introduced in its momentum and vice-versa. If  $\Delta x$  is the uncertainty in position and  $\Delta p$  be the uncertainty in its momentum, then according to Heisenberg, these quantities are related as follows :  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

In other words, it can be defined as :

*An expression of limits set by the wave nature of matter (electron) on finding the position and the state of motion of moving body (momentum) such that the product of uncertainties in simultaneous measurements of the position and momentum of a sub-atomic particle cannot be less than  $h/4\pi$ .*

Hence, in new atomic theory, an electron can not be regarded as having a fixed (definite) path around the nucleus, called orbits. It is a matter of probability that an electron is more likely to be found in one place or the other. So we can now visualise a region in space (diffused cloud) surrounding the nucleus, where the probability of finding the electron is maximum. Such a region is called as an **orbital**. It can be defined as :

*“ The electron distribution described by a wave function and associated with a particular energy.”*

- The new theory still defines a definite energy to an orbital in an atom (*a remarkable and accepted feature of Bohr's model*). The new theory abandons the concept of sharply defined paths.
- If we consider an electron moving in a circular orbit around the nucleus, then the wave train associated with the electron is shown in the figure.

If the two ends of the electron wave meet to give a regular series of crests and troughs, the electron wave is said to be *in phase*.

$$n'\lambda = 2\pi r$$

where  $n'$  is the number of waves made by an electron in that Bohr orbit

$$\Rightarrow \text{The number of waves made by the electron} = \frac{\text{circumference of the orbit}}{\text{wavelength}}$$

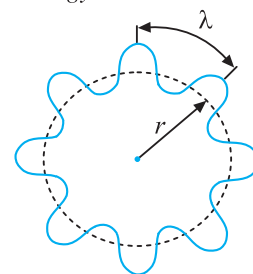
$$\begin{aligned} \text{Thus, } n' &= \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} & \left[ \because \lambda = \frac{h}{mv} \right] \\ &= \frac{2\pi}{h} (mvr) = \frac{2\pi}{h} \left( \frac{nh}{2\pi} \right) = n & \left[ \because mvr = \frac{nh}{2\pi} \right] \end{aligned}$$

Hence the number of waves ( $n'$ ) made by an electron in an orbit is equal to principal quantum number ( $n$ )

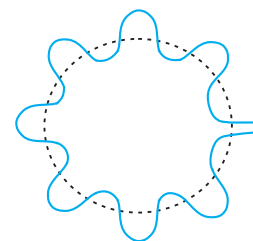
### Illustrating the concept :

*Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.*

Using the above result, the number of waves made by the electron in 3rd Bohr orbit is 3 (i.e.  $n' = 3$ ).



Electron wave in phase



Electron wave out of phase



**Illustration - 13** An electron is accelerated through a potential difference of  $V$  volts. Find the de Broglie wavelength associated with the electron.

**SOLUTION :**

When the electron is accelerated through a potential difference of  $V$  volts, it acquires a kinetic energy given by  $E = qV$ , where  $q$  is the charge on the electron. Also,

if  $m$  be its mass and  $v$  be the velocity then,  $E = \frac{1}{2}mv^2$

$$\Rightarrow v = \sqrt{\frac{2E}{m}}$$

$$\text{And de Broglie wavelength } (\lambda) = \frac{h}{mv} = \frac{h}{\sqrt{2Em}}$$

**Note :** The above result can be used directly, whenever required.

$$\text{In the given case, } E = qV \Rightarrow \lambda = \frac{h}{\sqrt{2(qV)m}}$$

**Illustration - 14** Calculate the uncertainty in position assuming uncertainty in momentum within 0.1 % for :

(a) a tennis ball weighing 0.2 kg and moving with a velocity of 10 m/s.

(b) a electron moving in an atom with a velocity of  $2 \times 10^6$  m/s.

**SOLUTION :**

Using Uncertainty Principle,

$$\Delta x \cdot \Delta p = \frac{h}{4\pi}$$

(a)  $p = mv = 0.2 \times 10 = 2.0 \text{ Kg m/s}$

$\Delta p = 0.1\% \text{ of } p = 2 \times 10^{-3}$

$$\Rightarrow \Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 2 \times 10^{-3}} \\ = 2.63 \times 10^{-32} \text{ m.}$$

(b) For an electron,  $p = m v$

$$p = 9.1 \times 10^{-31} \times (2 \times 10^6) \\ = 1.82 \times 10^{-24} \text{ Kg m/s}$$

$\Delta p = 0.1\% \text{ of } p = 1.82 \times 10^{-27} \text{ Kg m/s}$

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.82 \times 10^{-27}}$$

$$\Rightarrow \Delta x = 2.89 \times 10^{-8} \text{ m}$$

**Note :** This shows that for sub-atomic (microscopic) particles, Heisenberg's Principle is highly meaningful, as  $\Delta x$  is greater than their atomic radius.

## CONCEPT OF QUANTUM NUMBERS

## SECTION - 6

## Introduction to Quantum Mechanics

## Macroscopic Objects :

Motion of these objects *can be* described/calculated using classical mechanics (based on Newton's law of motion).

## Microscopic Objects

Motion of these objects *can not be* described/calculated using classical mechanics (based on Newton's law of motion).

- (i) Dual nature of matter is not considered in classical mechanics, so there is a need for Quantum Mechanics (takes into consideration the dual nature of matter).
- (ii) Quantum mechanics can also be applied on macroscopic objects (we can ignore their wave like properties) and still get the same results as Classical Mechanics.

## Equation of Quantum Mechanics :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

It defines the laws of motion that microscopic objects must obey.

Schrödinger equation is the governing equation of Quantum Mechanics. It is a complex equation and difficult to understand and solve with the knowledge of mathematics in classes XI and XII.

For a system whose energy doesn't vary with time, Schrödinger equation can be represented as :

$$\hat{H} \psi = E \psi$$

where  $\hat{H}$  = Hamiltonian operator (a mathematical operator).

$\psi$  = Wave function.

$E$  = Energy.

Schrödinger equation is relatively easier to construct. For a H-atom, when this equation is solved, it gives the energy levels for the electrons and corresponding wave function ( $\psi$ ) of the electron associated with each energy level.

What is a wave function ( $\psi$ ) ?

- It is a mathematical function whose value depends upon the coordinates of the electron in the atom.
- It doesn't have any physical significance.
- It is characterized (represented) by set of three quantum numbers ( $n$  : Principal quantum number,  $\ell$  : Azimuthal quantum number and  $m_\ell$  : Magnetic quantum number).

*Basically, it contains all the information about the electron.*

- Note :**
- Schrödinger equation can not be solved exactly for multi-electron atom (but can be solved approximately).
  - In case of single electron atom, energy of the orbital depends only on the principal quantum number ( $n$ ) but in case of multi-electron atom, it depends on ' $n$ ' as well as  $\ell$ .

### Designation of An Electron in an Orbital

An orbital is basically designated by three quantum numbers  $n$ ,  $\ell$  and  $m_\ell$  as defined below :

**(i) Principal Quantum Number ( $n$ ) :**

It is a positive integer with values of  $n = 1, 2, 3, \dots$ . In other way, it can also be designated with letters as K ( $n = 1$ ), L ( $n = 2$ ), M ( $n = 3$ ),  $\dots$ .

**Significance :**

- (a) It determines the size and energy of the orbital.

**Note :** For H and H-like species, orbital size and energy depends only on ' $n$ ' but for multi electron species, orbital energy depends on both ' $n$ ' and ' $\ell$ '.

- (b) It is also used to calculate the number of orbitals given by ' $n^2$ '. Thus, the maximum number of electrons in a shell (i.e. energy level as designated with letters as K, L, M etc.) are given by ' $2n^2$ ', since one orbital can at the maximum contains two electrons.

- As we have learnt in Bohr Model, increasing ' $n$ ' increases the energy of the electron, thus, energy of the orbital increases.
- Also, we have learnt that size of the energy shells increases with increasing ' $n$ '. Thus, we can expect the orbital size to increase with ' $n$ '.

- (ii) Azimuthal Quantum Number ( $\ell$ ) :** It is an integer having all values between 0 and  $n - 1$ . It is also known as orbital angular momentum quantum number or subsidiary quantum number.

**Significance :**

- (a) It is used to define the shape of an orbital.
- (b) It is used to represent a subshell (Each shell has subshells equal to shell number). A subshell can be thought of as sub-energy level inside an energy level.

**For example :**  $n = 1$  (K shell) has only one subshell ( $\ell = 0$ )

$n = 2$  (L shell) has two subshells ( $\ell = 0, 1$ )

And so on  $\dots$

Each value of ' $\ell$ ' can be designated with letters as s ( $\ell = 0$ ), p ( $\ell = 1$ ), d ( $\ell = 2$ ), f ( $\ell = 3$ ), g ( $\ell = 4$ ) and so on  $\dots$

We can create the following notation :

$$\begin{array}{llll}
 n = 1, & \ell = 0 & \Rightarrow & 1s \\
 n = 2, & \ell = 0, 1 & \Rightarrow & 2s, 2p \\
 n = 3, & \ell = 0, 1, 2 & \Rightarrow & 3s, 3p, 3d \quad \text{and so on } \dots
 \end{array}$$

(iii) **Magnetic Quantum Number ( $m_\ell$ ) :**

It is an integer having values between  $-\ell$  to  $+\ell$  including zero.

**Significance :**

(a) It gives information about the orientation of an orbital with respect to coordinate axis.

- **For example :** 's' orbital is spherical in shape. So, it can be oriented only in one way in space, hence only one orbital is possible.

**Note :** Number of orbitals in a sub-shell  $\equiv$  Number of possible orientations of an orbital.

- 'p' orbital has lobes above and below the plane as shown on page 29.

'p' subshell can be oriented in three ways (lobes can be along X, Y and Z axes).

Thus, three orbitals are possible in a p-subshell.

In general, number of orbitals in a sub-shell  $= 2\ell + 1$

Thus, 's' - subshell ( $\ell = 0$ ) has  $2(0) + 1 = 1$  orbital

'p' - subshell ( $\ell = 1$ ) has  $2(1) + 1 = 3$  orbital

Subshell	$\ell$	No. of orbitals	Max. e's per subshell	Possible values of $m_\ell$
s	0	1	2	0
p	1	3	6	-1, 0, 1
d	2	5	10	-2, -1, 0, 1, 2
f	3	7	14	-3, -2, -1, 0, 1, 2, 3

Note the conventions :

's' - subshell

$m_\ell = 0$

'p' - subshell

Orbitals	$m_\ell$
$p_x$	+1 or -1
$p_y$	+1 or -1
$p_z$	0

'd' - subshell

Orbitals	$m_\ell$
$d_{xy}$	$\pm 2$
$d_{yz}$	$\pm 1$
$d_{zx}$	$\pm 1$
$d_{x^2 - y^2}$	$\pm 2$
$d_{z^2}$	0

**Note :**  $n, \ell, m_\ell$  are the solutions of Schrödinger equation. There is another quantum number known as spin quantum number ( $m_s$ ) which has been obtained experimentally.

There is an orbital angular momentum associated with an electron in subshell as given below.

*It depends on both Azimuthal and Magnetic quantum numbers.*

$$L = \sqrt{\ell(\ell+1)} \frac{h}{2\pi} \equiv \sqrt{\ell(\ell+1)} \hbar \quad (\text{where } \hbar = \frac{h}{2\pi} = \text{reduced Planck's constant})$$

**Spin Quantum number ( $m_s$ ) :** This quantum number accounts for the spin of electron about its axis similar to earth's motion about the sun as well as about its own axis.

An orbital can have a maximum of two electrons spinning in opposite directions leading to a spin angular momentum (vector quantity).

Thus, for two electron in an orbital,  $m_s = +\frac{1}{2}$  (spin anticlockwise)  $\equiv \uparrow$  ;  $m_s = -\frac{1}{2}$  (spin clockwise)  $\equiv \downarrow$

Magnitude of spin angular momentum is given by :

$$\sqrt{s(s+1)} \frac{h}{2\pi} \equiv \frac{\sqrt{3}}{2} \frac{h}{2\pi} \quad \left( s = \frac{1}{2} \text{ for an electron} \right) \equiv \frac{\sqrt{3}}{2} \hbar \quad \left( \hbar = \frac{h}{2\pi} = \text{reduced planck's constant} \right)$$

**Note :**  $m_s = \frac{1}{2}$  for any electron. In an orbital,  $m_s = \pm \frac{1}{2}$  has been taken so as to distinguish the two electrons in it.

spin quantum number has no classical analogue.

### Difference between Orbit and Orbital :

Orbit	Orbital
<ol style="list-style-type: none"> <li>1. It is circular path around the nucleus in which an electron moves.</li> <li>2. It is characterized by <math>n</math>.</li> <li>3. It has no real meaning.</li> </ol>	<ol style="list-style-type: none"> <li>1. It is a quantum mechanical concept and refers to one electron wave.</li> <li>2. It is characterized by <math>n, \ell, m_\ell</math>.</li> <li>3. It represents the probability of finding an electron at any point (through <math> \psi ^2</math>).</li> </ol>

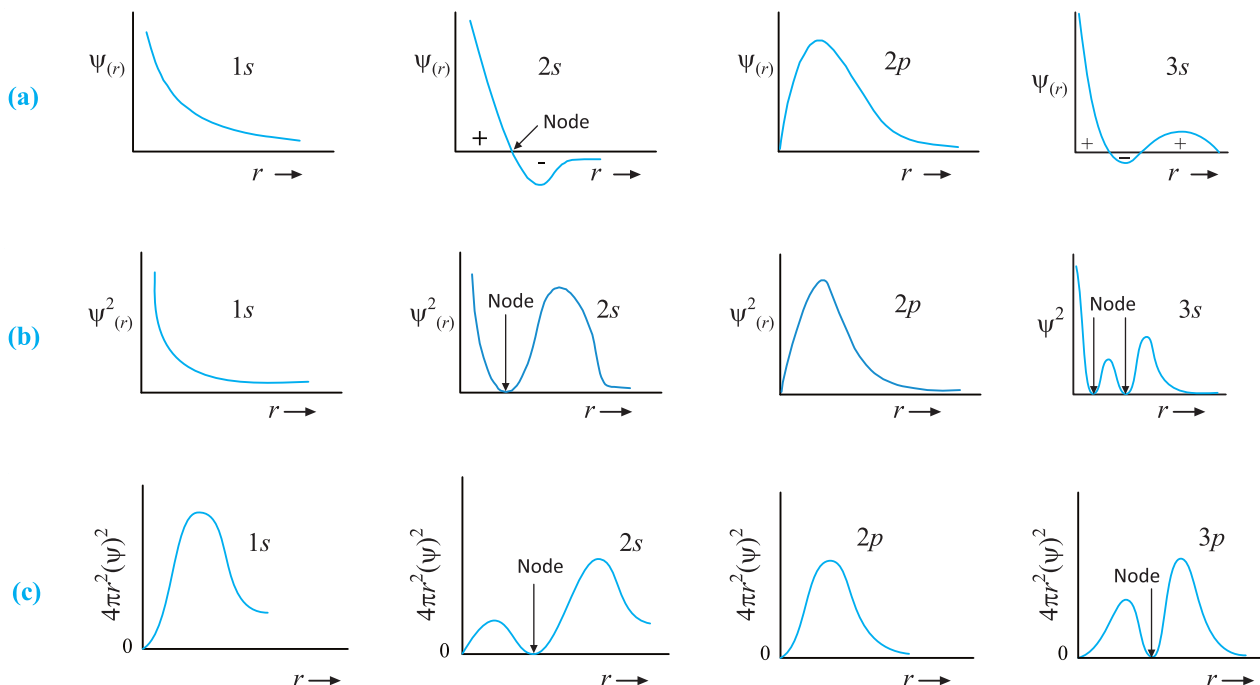
### Hydrogen Atom and the Schrodinger Equation:

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electrons can occupy and the corresponding wave function(s) ( $\psi$ ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number  $n$ , azimuthal quantum number  $l$  and magnetic quantum number  $m_l$ ) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the  $|\psi|^2$  at that point.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen only on the quantum number  $n$ , the energies of the orbitals in multi-electron atoms depend on quantum numbers  $n$  and  $l$ .

### Plots of Radial Wave Function $R(r)$ , Radial Probability Density $R^2(r)$ and Radial Probability Function $[4\pi r^2 R^2]$

**Vs 'r':** The probability of finding the electron in a spherical shell of thickness  $dr$  at a distance  $r$  from the nucleus is equal to the product of the volume of shell of thickness  $dr$  at distance  $r$  from the nucleus ( $4\pi r^2 dr$ ) and the radial probability density  $R^2(r)$  per unit volume i.e., equal to  $4\pi r^2 R^2(r) dr = P dr$  where  $P = 4\pi r^2 R^2(r)$  is called Radial Probability Function.



- In the plots of radial probability versus distance from the nucleus, number of peaks i.e. region of maximum probability =  $n - 1$  for instance, 2s has two peaks 3s will have 3 peaks, 2p has one peak, 3p has two peaks and so on.

As we see from the above graph,  $\Psi^2$  decreases and approaches to zero as  $r$  increases. Region where  $\Psi^2$  reduces to zero is called **nodal surface** (nodes). A **node** is a region of space where probability of finding the electron is zero. There are also **angular nodes** (**nodal plane**) which represents plane passing through nucleus and having probability density function as zero.

For a hydrogen like atom wave function, of principal quantum number  $n$ , there are

- (i)  $(n - \ell - 1)$  radial nodes
- (ii)  $\ell$  angular nodes
- (iii)  $(n - 1)$  total nodes.

Thus :

- 2s has one node. 3s has two nodes and so on.
- 1s ( $n = 1, \ell = 0$ ) subshell is without any node.
- 2s ( $n = 2, \ell = 0$ ) subshell will have only one radial node, while 2p ( $n = 2, \ell = 1$ ) subshell will have only one angular node.
- 3s ( $n = 3, \ell = 0$ ) subshell will have two radial nodes, 3p ( $n = 3, \ell = 1$ ) subshell will have one radial and one angular node while 3d ( $n = 3, \ell = 2$ ) will have two angular nodes.

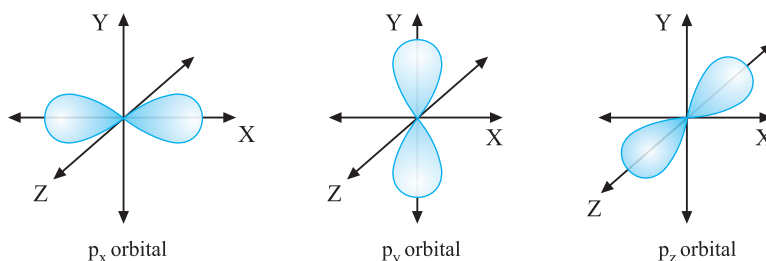
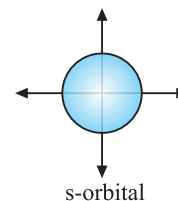


**Boundary surface diagram :** It is surface (contour) which represents a constant  $|\psi|^2$ . In general, it is the region where the probability of finding the electron is 90%.

As mentioned earlier, the 's' orbitals are spherical in shape which means that the probability of finding the electron at a given distance is equal in all the direction.

Also, the size of these orbitals increases as 'n' increases.

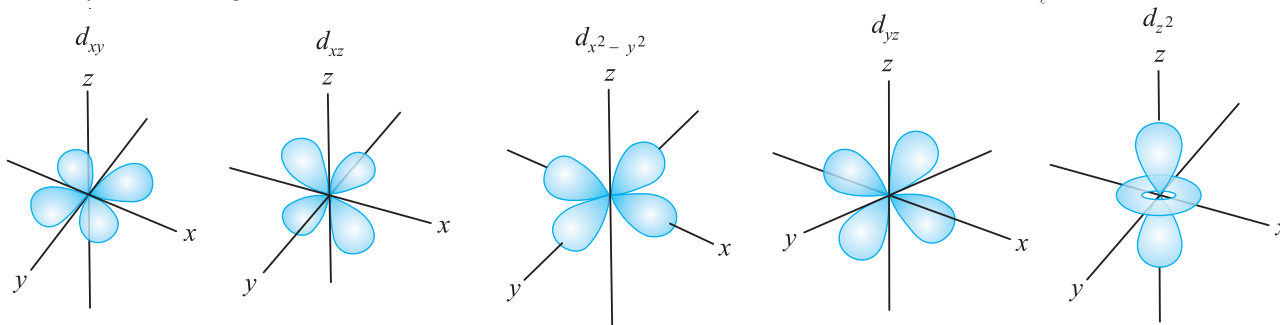
Boundary Surface Diagrams of p-orbitals are not spherical as shown :



As we can see, there are two lobes on either side of the plane passing through the nucleus having probability of finding the electron as zero on it.

- All three orbital have same shapes and energy.
- Here also, energy of these orbitals increases with increasing 'n'.
- No. of radial nodes (for p-orbitals) are given by  $n - 2$

Boundary Surface Diagrams of d-orbitals are shown below. For d-subshells, there are 5 values of  $m_\ell$ . Thus, d has 5 orbitals.



### Energy of orbitals :

- For H-atom, energy of an orbital can be solely calculated by using 'n'  
Thus,  $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$   
Orbitals having same energy are called degenerate orbitals.
- For an atom containing multi electrons, energy of an electron depends on 'n' as well as ' $\ell$ '.

In this case, each  $e^-$  is attracted by the nucleus but is repelled by every other electron. The electrons in the outer shell experiences less attractive force as there is a partial screening of positive charge known as shielding of the outer shell electrons from the nucleus.

- 's' orbitals are more tightly bound to nucleus than p orbitals, p orbitals are more tightly bound to nucleus than d orbitals and so on. Thus, energy of 's' orbitals is more negative than p-orbitals.

**Illustration - 15**

*In all, how many nodal planes are there in the atomic orbitals for the principal quantum number  $n = 3$ .*

**SOLUTION :**

Shell with  $n = 3$  has 1 's' (3s), 3 'p' ( $p_x, p_y, p_z$ ) and 5

'd' ( $d_{xy}, d_{xz}, d_{yz}, d_{(x^2-y^2)}$  and  $d_z^2$ ) orbitals.

- 's' has no nodal plane.
- Each of  $p_x, p_y, p_z$  has one nodal plane, which means a total of 3 nodal planes.
- $d_z^2$  has no nodal plane.

Each of  $d_{xy}, d_{xz}, d_{yz}, d_{(x^2-y^2)}$  has 2 nodal planes, which means a total of 8 nodal planes.

Hence for  $n = 3$ , a total of 11 nodal planes are there.

**Illustration - 16**

*The wave function ( $\psi$ ) of 2s-orbital is given by :  $\psi_{2s} = \frac{1}{\sqrt{32\pi}} \left[ \frac{1}{a_0} \right]^{3/2} \left[ 2 - \frac{r}{a_0} \right] e^{-r/2a_0}$*

*At  $r = r_0$ , radial node is formed. Calculate  $r_0$  in terms of  $a_0$ .*

**SOLUTION :**

For radial node at  $r = r_0$ ,  $\psi_{2s}^2 = 0$ . This is possible only when  $\left[ 2 - \frac{r_0}{a_0} \right] = 0 \quad \therefore r_0 = 2a_0$

## ELECTRONIC CONFIGURATION OF ELEMENTS

## SECTION - 7

Quantum numbers can now characterise the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules and selective principles are used. The distribution of electrons in an atom is known as *the electronic configuration of that element*.

Electronic configuration of an element is represented by the notation  $n \ell^x$  :

$n$  : principal quantum number     $\ell$  : denotes the sub-shell     $x$  : number of electrons present in an orbital

**Aufbau Principle**

An atom in its lowest state of energy is said to be in *ground state*. The ground state is the most stable state in an atom. According to Aufbau principle:

*"electrons are added progressively to the various orbitals in their order of increasing energy starting with the orbital of lowest energy"*

The order of increasing energy may be summed up as : 1s, 2s, 2p, 3s, 3p, **4s, 3d**, 4p, **5s, 4d**, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,.....

As a working rule, a new electron enters an empty orbital for which the value of  $(n + \ell)$  is minimum. If the value of  $(n + \ell)$  is same for two or more orbitals, the new electron enters an orbital having lower value of  $n$ .

**Pauli Exclusion Principle**

According to this principle :

*"no two electrons in an atom can have the same set of all the quantum numbers. or one can say that no two electrons can have the same quantised states."*

Consider an electronic arrangement in 1st energy level ( $n = 1$ ). For  $n = 1$ ,  $\ell = 0$ , and  $m_\ell = 0$ . Now  $m_s$  can have two values corresponding to each value of  $m_\ell$  i.e.  $m_s = +1/2, -1/2$ . Hence the possible designation of an electron in a state with  $n = 1$  is  $(1, 0, 0, +1/2)$  and  $(1, 0, 0, -1/2) \equiv (n, \ell, m_\ell, m_s)$  i.e., two quantised states. This implies that an orbital can accommodate (for  $n = 1, m_\ell = 0$ , i.e., one orbital) maximum of two electrons having opposite spins.

The maximum number of electrons in the different sub-shells are :

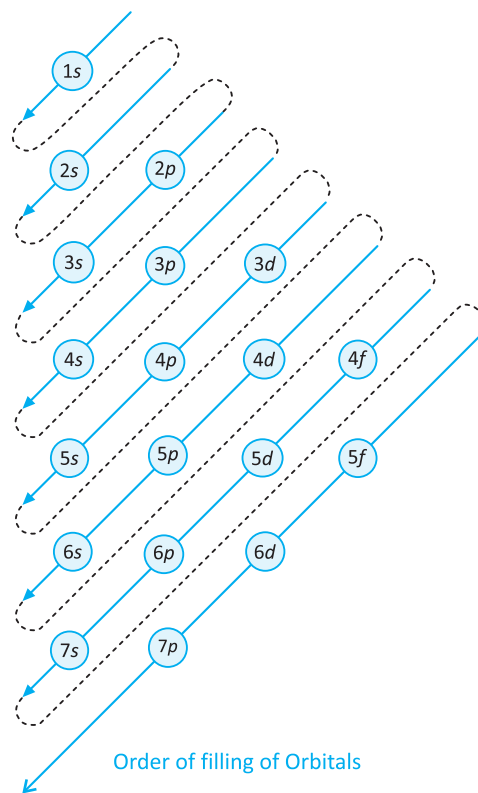
$s$  sub-shell = 2,  $p$  sub-shell = 6,  $d$  sub-shell = 10 and  $f$  sub-shell = 14.

**Hund's Rule Of Maximum Multiplicity**

According to this rule : *"electrons never pair until no available empty degenerate orbitals are left to them."*

This means an electron always occupies a vacant orbital in the same sub-shell (degenerate orbital) and pairing starts only when all of the degenerate orbitals are filled up. This means that the pairing starts with 2nd electron in  $s$  sub-shell, 4th electron in  $p$  sub-shell, 6th electron in  $d$  sub-shell and 8th electron in  $f$  sub-shell.

By doing this, the electrons stay as far away from each other as possible. This is highly reasonable if we consider the *electron-electron repulsion*. Hence electrons obey Hund's rule as it results in lower energy state and hence more stability.



### Extra Stability of Half And Fully Filled Orbitals

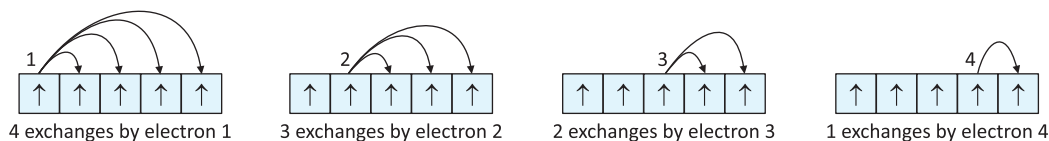
A particularly stable system is obtained when a set of equivalent orbitals (degenerate orbitals) is either fully filled or half filled, i.e., each containing one or a pair of electrons. This effect is more dominant in *d* and *f* sub-shells.

This means three or six electrons in *p* sub-shell, five or ten electrons in *d* sub-shell, and seven or fourteen electrons in *f* sub-shell forms a stable arrangement. Note this effect when filling of electrons takes place in *d* sub-shells (for atomic numbers  $Z = 24, 25$  and  $29, 30$ ).

### Stability of Completely Filled and Half filled subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most atoms follow the basic rules given in the sections written above. However, in certain elements such as Cr and Cu where the two lower subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshells of higher energy getting either completely filled or half filled. The valence electronic configuration of Cr and Cu therefore are  $4s^1 3d^5$  and  $4s^1 3d^{10}$  respectively and not  $4s^2 3d^4$  and  $4s^2 3d^9$ . It has been found that there is extra stability associated with these electronic configurations. This stabilization is due to the following factors:

- **Symmetrical Distribution of electrons:** It is well known that symmetry leads to stability. The completely filled or half filled sub shells have a symmetric distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here 3d) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and electrons are more strongly attracted by the nucleus.
- **Exchange Energy:** The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and energy released due to this exchange is called Exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability.



Possible exchanges for a  $d^5$  configuration

**Illustration - 17** A compound of Vanadium has a magnetic moment of 1.73 B.M. Work out the electronic configuration of vanadium in the compound.

#### SOLUTION :

The magnitude of magnetic moment ( $\mu$ ) of a compound/ species/ion is given by :  $\mu = \sqrt{n(n+2)} \text{ B.M.}$

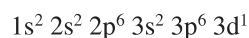
( $n$  = number of unpaired electrons ; BM : unit of magnetic moment in Bohr's Magnetron)

$$\Rightarrow 1.73 = \sqrt{n(n+2)}$$

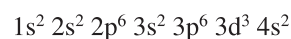
On solving for  $n$ , we get  $n = 1$ . This means that vanadium ion ( $Z = 23$ ) in the compound has one unpaired electron.



So its electronic configuration (e.c.) must be :



i.e., vanadium exists as  $V^{4+}$  ion in the compound since the ground state e.c. of  ${}_{23}\text{V}$  is :



**Note :** In these kind of questions, keep on removing  $e^-$  from the outermost orbitals.

**Illustration - 18** Write down the electronic configuration of following species. Also find the number of unpaired electrons in each. (a) Fe, Fe<sup>2+</sup>, Fe<sup>3+</sup> (Z of Fe = 26), (b) Br, Br<sup>-</sup> (Z of Br = 35), (c) V, V<sup>3+</sup> (Z of V = 23)

**SOLUTION :**

Follow the order of increasing energy (Aufbau Rule) :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d,.....

(a) Fe(Z = 26): 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>6</sup>

Note that 3d orbital are not fully filled.



Orbitals filled as per Hund's Rule.

Clearly the number of unpaired electrons is 4.

➤ Fe<sup>2+</sup> : (Z = 26) [No. of electrons = 24]

While writing electronic configuration (e.c.) of cations, first write e.c. of neutral atom and then "remove desired number of electrons from outermost orbital".

In Fe<sup>2+</sup>, remove 2e<sup>-</sup> from 4s<sup>2</sup> since 4s orbital (through lower in energy than 3d) is the outermost. Hence e.c. of Fe<sup>2+</sup> is: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>6</sup> 4s<sup>0</sup>

Note that number of unpaired electrons remains same as that in Fe, i.e. 4.

➤ Fe<sup>3+</sup> (Z = 26) [No. of electrons = 23]

Now remove 2e<sup>-</sup> from 4s<sup>2</sup> and 1e<sup>-</sup> from 3d<sup>6</sup> to get e.c. as : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup> 4s<sup>0</sup>

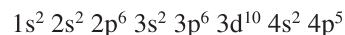
Note that, now all 'd' orbits have an odd electron (i.e. are half filled).



Hence number of unpaired electrons in Fe<sup>3+</sup> = 5.

(b) Br (Z = 35) [No. of electron = 35]

Following Aufbau rule, e.c. is :



Clearly one of 4p<sup>5</sup> orbitals contains unpaired electrons: 4p<sup>5</sup> ≡



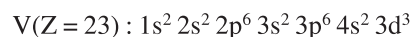
Orbitals filled as per Hund's Rule.

Hence Br has only one unpaired electron.

➤ Br<sup>-</sup> (Z = 35) [No. of electron = 36]

Since anion(s) is(are) formed by adding electron(s), so simply write e.c. as per total number of electrons finally. For Z = 35, e.c. is : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup>  
Clearly there are no unpaired electrons.

(c) Following on pattern in (a), we can write e.c. for V as follows.

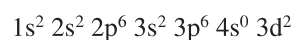


Orbitals filled as per Hund's Rule.

⇒ 3 unpaired electrons.

➤ V<sup>3+</sup> (Z = 23) [No. of electron = 20]

Remove 3e<sup>-</sup> from outermost orbitals successively i.e., '2e<sup>-</sup>' from 4s<sup>2</sup> and 1e<sup>-</sup> from 3d<sup>3</sup>. Hence e.c. of V<sup>3+</sup> is :



Orbitals filled as per Hund's Rule.

⇒ 2 unpaired electrons.

## MISCELLANEOUS ILLUSTRATIONS

**Illustration - 19** Find the threshold wavelength for a copper plate, a sodium plate and cesium plate. The work functions of these plates are : 4.5 eV, 2.3 eV & 1.9 eV respectively.

**SOLUTION :**

Use  $\lambda_0 = \frac{hc}{E}$   $E \rightarrow$  stopping energy.

For sodium  $\lambda_0 = \frac{1242 \text{ eV} \cdot \text{nm}}{4.5 \text{ eV}} = 540 \text{ nm}$

For copper  $\lambda_0 = \frac{1242 \text{ eV} \cdot \text{nm}}{4.5 \text{ eV}} = 276 \text{ nm}$

For caesium  $\lambda_0 = \frac{1242 \text{ eV} \cdot \text{nm}}{1.9 \text{ eV}} = 654 \text{ nm}$

**Illustration - 20** A UV light of wavelength 280 nm is used in an experiment on photoelectric effect with Li (work function = 2.5 eV) as cathode. Find :

- (a) the maximum KE of photoelectrons and (b) the stopping potential

**SOLUTION :**

- (a) The maximum K.E is :

$$K_{\max} = \frac{hc}{\lambda} - \phi = \frac{1242}{280} - 2.5 = 1.9 \text{ eV}$$

- (b) Stopping potential V is given by

$$V = \frac{K_{\max}}{e} = 1.9 \text{ V}$$

**Illustration - 21** (a) Find the wavelength of the radiation required to excite the electron in  $\text{Li}^{++}$  from the first to the third Bohr orbit.

- (b) How many spectral lines are observed in the emission spectrum of the above excited system ?

**SOLUTION :**

- (a) As we know  $E = -13.6 \frac{Z^2}{n^2} \text{ eV}$

So  $\Delta E = E_3 - E_1 = 8 \times 13.6 \text{ eV} = 108.8 \text{ eV}$ .

Use  $\lambda = \frac{1242 \text{ eV} \cdot \text{nm}}{108.8 \text{ eV}} = 11.4 \text{ nm}$

- (b) There are three lines in the spectrum.

**Illustration - 22** A hydrogen sample is prepared in a particular excited state A. Photons of energy 2.55 eV get absorbed into the sample to take some of the electrons to a further excited state B. Find the quantum numbers of the states A and B.

**SOLUTION :**

Use the energy difference diagram and we can see that 2.55 eV can only be absorbed in transition  $n = 2$  to  $n = 4$ . Hence the quantum numbers are 2 and 4.

**Illustration - 23** Find the wavelengths in a hydrogen spectrum between the range 500 nm to 700 nm.

**SOLUTION :**

First find energy of the photons having wavelength 500 nm and 700 nm.

$$E_{\lambda = 500} = \frac{1242 \text{ eV} \cdot \text{nm}}{500 \text{ nm}} = 2.44 \text{ eV}$$

$$E_{\lambda = 700} = \frac{1242 \text{ eV} \cdot \text{nm}}{700 \text{ nm}} = 1.77 \text{ eV}$$

Thus the energy difference should be between 1.77 eV and 2.44 eV.

The desired transition is  $3 \rightarrow 2$  for  $\Delta E = 1.9 \text{ eV}$ .

$$\text{Hence } \lambda = \frac{hc}{\Delta E} = \frac{1242 \text{ eV} \cdot \text{nm}}{1.9 \text{ eV}} = 654 \text{ nm}.$$

**Illustration - 24** A beam of ultraviolet radiation having wavelength between 100 nm and 200 nm is incident on a sample of atomic hydrogen gas. Assuming that the atoms are in ground state, which wavelengths will have low intensity in the transmitted beam? If the energy of a photon is equal to the difference between the energies of an excited state and the ground state, it has large probability of being absorbed by an atom in the ground state.

**SOLUTION :**

$$E_{\lambda=100 \text{ nm}} = \frac{1242 \text{ eV} \cdot \text{nm}}{100 \text{ nm}} = 12.42 \text{ eV}$$

And that corresponding to  $\lambda = 200 \text{ nm}$  is 6.21 eV

$$E_2 - E_1 = 10.2 \text{ eV} \quad \text{and} \quad E_3 - E_1 = 12.1 \text{ eV}$$

$$E_4 - E_1 = 12.75 \text{ eV}$$

Thus 10.2 eV and 12.1 eV have larger probability.

$$\Rightarrow \lambda_1 = \frac{1242 \text{ eV} \cdot \text{nm}}{10.2 \text{ eV}} = 122 \text{ nm}$$

$$\text{and } \lambda_2 = \frac{1242 \text{ eV} \cdot \text{nm}}{12.1 \text{ eV}} = 103 \text{ nm}$$

**Illustration - 25** Light corresponding to the transition  $n = 4$  to  $n = 2$  in hydrogen atoms falls on cesium metal (work function = 1.9 eV). Find the maximum kinetic energy of the photoelectrons emitted.

**SOLUTION :**

The energy of photons emitted in transition  $n = 4$  to  $n = 2$  is  $h\nu = 13.6 \text{ eV} \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 2.55 \text{ eV}$

$$K.E._{\text{max}} = 2.55 - 1.9 = 0.65 \text{ eV}$$

**Illustration - 26** Calculate the smallest wavelength of radiation that may be emitted by

- (a) hydrogen      (b)  $\text{He}^+$  and      (c)  $\text{Li}^{2+}$

**SOLUTION :**

Smallest wavelength will be from  $\infty \rightarrow 1$ .

$$\text{For H - atom } \frac{1}{\lambda} = RZ^2 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = R \quad \Rightarrow \quad \lambda = 911.5 \text{ \AA}$$

$$\text{For } \text{He}^+ \text{ ion } Z = 2 \quad \frac{1}{\lambda} = R \cdot Z^2 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) ; \quad \lambda = \frac{1}{4R}$$

$$\text{For } \text{Li}^{2+} ; Z = 3 \quad \frac{1}{\lambda} = R \cdot 3^2 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) ; \quad \lambda = \frac{1}{9R}$$

**Illustration - 27** Find the binding energy of a hydrogen atom in the state  $n = 2$ .

**SOLUTION :**

Binding energy will be  $13.6 \frac{Z^2}{n^2}$

$$\text{For } n = 2 ; \quad \text{B.E} = 13.6 \frac{1^2}{2^2} = 3.4 \text{ eV}$$



**Illustration - 28** Find the radius and energy of a  $\text{He}^+$  ion in the states

- (a)  $n = 1$       (b)  $n = 4$  and      (c)  $n = 10$ .

**SOLUTION :**

$$\text{Radius} = 52.9 \frac{n^2}{z} \text{ pm}$$

$$z = 2, n = 1 \Rightarrow r = 52.9 \times \frac{1^2}{2} = 26.45 \text{ pm}$$

$$r_4 = 52.9 \times \frac{4^2}{2} = 423.2 \text{ pm}$$

$$r_{n=10} = 52.9 \times \frac{10^2}{2} = 2645 \text{ pm}$$

**Illustration - 29** A positive ion having just one electron ejects it if a photon of wavelength  $228 \text{ \AA}$  or less is absorbed by it. Identify the ion.

**SOLUTION :**

First find  $\Delta E$  corresponding to this wavelength

$$\Delta E = \frac{1242}{22.8} = 54.47 \text{ eV}$$

$$\Rightarrow 54.47 = 13.6 z^2 \Rightarrow z = 2$$

Hence the ion is  $\text{He}^+$ .

**Illustration - 30** A hydrogen atom in state  $n = 6$  makes two successive transitions and reaches the ground state. In the first transition a photon of  $1.13 \text{ eV}$  is emitted.

- (a) Find the energy of the photon emitted in the second transition.  
 (b) What is the value of  $n$  in the intermediate state ?

**SOLUTION :**

Use the energy diagram

$$E_6 = -0.378$$

$$E_5 = -0.544$$

$$E_4 = -0.85$$

$$E_3 = -1.51$$

By looking at the energy gap value of  $1.13 \text{ eV}$ . We can see that intermediate state is  $3^{\text{rd}}$ .

Hence the second transition will be from  $3 \rightarrow 1$

$$\frac{1}{\lambda} = R \times 1^2 \times \left( \frac{1}{1^2} - \frac{1}{3^2} \right)$$

$$\frac{1}{\lambda} = \frac{8R}{9}$$

$$\lambda = \frac{9}{8R} = \frac{9}{8} \times 911.5 \text{ \AA} = 1024.4 \text{ \AA}$$

**Illustration - 31** A beam of light having wavelengths distributed uniformly between  $450 \text{ nm}$  to  $550 \text{ nm}$  passes through a sample of hydrogen gas. Which wavelength will have the least intensity in the transmitted beam ?

**SOLUTION :**

$$E_1 = \frac{hc}{450} = 2.76 \text{ eV} ; \quad E_2 = \frac{1242}{550} = 2.26 \text{ eV} \quad \text{Observing from the energy diagram} \rightarrow$$

Clearly, the intermediate wavelength absorbed will be corresponding to energy  $= 2.55 \text{ eV}$

Hence corresponding wavelength will be  $486 \text{ nm}$ .

$n = 4$	$-0.85 \text{ eV}$
$n = 3$	$-1.51 \text{ eV}$
$n = 2$	$-3.4 \text{ eV}$
$n = 1$	$E = -13.6 \text{ eV}$

$E_4 - E_2 = 2.55 \text{ eV}$

**Illustration - 32** A hydrogen atom in ground state absorbs a photon of ultraviolet radiation of wavelength 50 nm. Assuming that the entire photon energy is taken up by the electron, with what kinetic energy will the electron be ejected ?

**SOLUTION :**

Visualise the given situation corresponding to a photoelectric effect.

$$\text{Energy corresponding to 50 nm wavelength} = \frac{1242}{50} = 24.84 \text{ eV}$$

The ionization energy of hydrogen atom in ground state is 13.6 eV which is equivalent to work function of hydrogen atom.

$$\text{Hence, K.E. of electron ejected} = 24.84 - 13.6 = 11.24 \text{ eV.}$$

**IN-CHAPTER EXERCISE - C**

- Calculate the wavelength of electron associated with energy of 1.0 electron volt.
- A moving particle is associated with wavelength  $5 \times 10^{-8} \text{ m}$ . If its momentum is reduced to half of its value, compute the new wavelength.
- Calculate the magnetic moments ( $\mu$ ) for the atoms having atomic numbers, 7, 24, 34, 36. Also identify the atoms.
- Given below are the sets of quantum numbers for the given orbitals ( $n, \ell, m_\ell$ ). Name these orbitals.  
(a) (2, 1, -1)      (b) (4, 2, 0)      (c) (3, 1, 0)      (d) (3, 2,  $\pm 2$ )      (e) (4, 1,  $\pm 1$ )
- What values are assigned to quantum numbers  $n, \ell, m_\ell$  for :  $2s, 2p_z, 4d_{(x^2-y^2)}, 4d_{(z^2)}$
- Write down the electronic configurations of the following and also determine the number of unpaired electrons in each.  
 $\text{Al, Ar, Ni}^{2+}, \text{Cl, Cl}^-, \text{Cr, Cr}^{3+}, \text{Ni}^{2+}, \text{Mn, Mn}^{2+}, \text{Mn}^{4+}$
- Determine the orbital angular momentum of an electron in :  $4s, 3p, 3d$ .
- Calculate the uncertainty in velocity of an electron if the uncertainty in its position is of the order of 0.1 nm.

**Choose the correct option(s) for each of the following.**

- The orbital angular momentum of an electron in  $2s$  orbital is :  
(A)  $+\frac{1}{2} \frac{h}{2\pi}$       (B) zero      (C)  $\frac{h}{2\pi}$       (D)  $\sqrt{2} \frac{h}{2\pi}$
- Number of electrons that F ( $Z = 9$ ) has in  $p$ -orbitals is equal to :  
(A) number of electrons in  $s$ -orbitals in Na (11e)      (B) number of electrons in  $d$ -orbitals in  $\text{Fe}^{3+}$  (23e)  
(C) number of electrons in  $d$ -orbitals in Mn (25e)      (D) (A), (B) and (C) true
- The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order :  
(A)  $10^{-10} \text{ m}$       (B)  $10^{-20} \text{ m}$       (C)  $10^{-30} \text{ m}$       (D)  $10^{-40} \text{ m}$
- Which orbital gives an electron a greater probability of being found close to the nucleus ?  
(A)  $3p$       (B)  $3d$       (C)  $3s$       (D) equal
- The correct set of four quantum numbers for the valence electron of rubidium ( $Z = 37$ ) is :  
(A)  $n = 5, \ell = 0, m = 0, m_s = +1/2$       (B)  $n = 5, \ell = 1, m = 0, m_s = +1/2$   
(C)  $n = 5, \ell = 1, m = 1, m_s = +1/2$       (D)  $n = 6, \ell = 0, m = 0, m_s = +1/2$
- For a  $d$ -electron the orbital angular momentum is : ( $\hbar = h/2\pi$ )  
(A)  $\sqrt{6}\hbar$       (B)  $\sqrt{2}\hbar$       (C)  $\hbar$       (D)  $2\hbar$

15. The correct set of quantum numbers for the unpaired electron of chlorine atoms is :  
 (A)  $n = 2, \ell = 1, m_\ell = 0$  (B)  $n = 2, \ell = 1, m_\ell = 1$   
 (C)  $n = 3, \ell = 1, m_\ell = 1$  (D)  $n = 3, \ell = 0, m_\ell = 0$
16. How many number of atomic orbitals associated with M-shell ?  
 (A) 9 (B) 12 (C) 16 (D) 25
17. In hydrogen atom an orbit has a diameter of about  $16.92 \text{ \AA}$ , what is the maximum number of electrons that can be accommodated ?  
 (A) 8 (B) 32 (C) 50 (D) 72
18. In any sub-shell maximum number of electrons having same value of spin quantum number is :  
 (A)  $\sqrt{\ell(\ell + 1)}$  (B)  $\ell$  (C)  $2\ell + 1$  (D)  $4\ell + 1$
- \*19. Which of the following sets of quantum number(s) is(are) not possible ?
- |     | $n$ | $\ell$ | $m_\ell$ | $m_s$ |     | $n$ | $\ell$ | $m_\ell$ | $m_s$ |
|-----|-----|--------|----------|-------|-----|-----|--------|----------|-------|
| (A) | 4   | 2      | -2       | +1/2  | (B) | 3   | 0      | 0        | -1/2  |
| (C) | 3   | 2      | -3       | -1/2  | (D) | 5   | 3      | 0        | +1/2  |
20. Which have the same number of s-electrons as the d-electrons in  $\text{Fe}^{2+}$  ?  
 (A) Li (B) Na (C) N (D) P
21. Hund's rule deals with the distribution of electrons in :  
 (A) a quantum shell (B) an orbit  
 (C) an orbital (D) degenerate orbitals
22. Which one of the following orbitals is nearest to the nucleus ?  
 (A) 4f (B) 5d (C) 6s (D) 7p
- \*23. Which cannot be the correct value of angular momentum ?  
 (A)  $2\hbar$  (B)  $1.5 \frac{\hbar}{\pi}$  (C)  $2.5\hbar$  (D)  $0.5 \frac{\hbar}{\pi}$
24. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon ?  
 (A) 3s (B) 2p (C) 2s (D) 1s
25. Which of the following arrangements of electrons is mostly likely to be stable ?
- |     |          |     |          |
|-----|----------|-----|----------|
| (A) | $3d$<br> | (B) | $3d$<br> |
| (C) | $3d$<br> | (D) | $3d$<br> |
26. Which of the following orbitals has/have zero probability of finding the electron in xy-plane ?  
 (A)  $p_z$  (B)  $d_{yz}$  (C)  $d_{zx}$  (D)  $p_x$
27. Which of the following statements about nodal planes are not true ?  
 (A) A plane on which there is zero probability that the electron will be found  
 (B) A plane on which there is maximum probability that the electron will be found  
 (C) Both  
 (D) None of these

## Electronic Configurations of the Elements

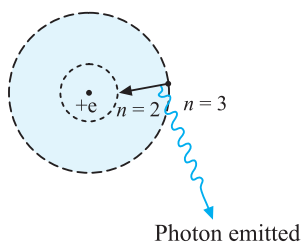
Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

\*Elements with exceptional electronic configurations

## SUBJECTIVE SOLVED EXAMPLES

**Example - 1** Calculate the wavelength and wave number of the spectral line when an electron in H-atom falls from higher energy state  $n = 3$  to a state  $n = 2$ . Also determine the energy of a photon to ionize this atom by removing the electron from 2nd Bohr's orbit. Compare it with the energy of photon required to ionize the atom by removing the electron from the ground state.

**SOLUTION :**



First calculate the energy ( $\Delta E$ ) between the Bohr orbits  $n = 3$  and  $n = 2$  using :

$$\Delta E = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV}$$

$$\Delta E_{(3 \rightarrow 2)} = 13.6 (1)^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \text{ eV}$$

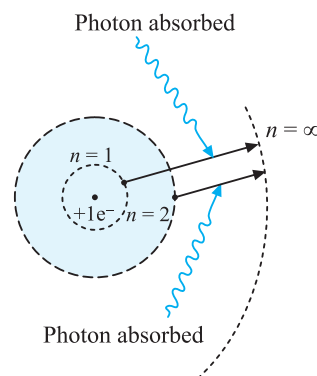
$$= 1.89 \text{ eV}$$

Now this energy difference is the energy of the photon emitted.

$$\Rightarrow E_{\text{photon}} = \frac{12400}{\lambda \text{ (in } \text{\AA})} \text{ eV}$$

$$\Rightarrow \lambda = \frac{12400}{1.89} = 6560.3 \text{ \AA}$$

and  $\bar{\nu} = \frac{1}{\lambda} = 1.52 \times 10^6 \text{ m}^{-1}$



- To ionize the atom from  $n = 2$ , the transition will be  $n = 2 \rightarrow n = \infty$ .

$$\Delta E_{(2 \rightarrow \infty)} = 13.6 \times 1^2 \times \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{ eV}$$

$$= 3.4 \text{ eV}$$

- To ionize the atom from ground state ( $n = 1$ ), the transition is  $1 \rightarrow \infty$ .

$$\Delta E = 13.6 \text{ eV} \times 1^2 \times \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = 13.6 \text{ eV}$$

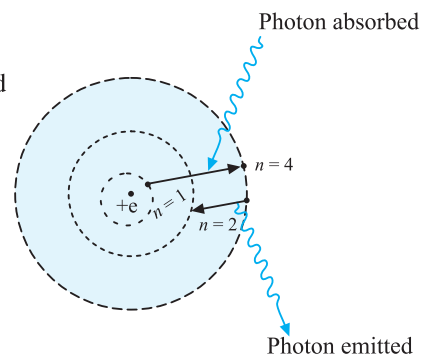
**Example - 2** A hydrogen atom in the ground state is hit by a photon exciting the electron to 3rd excited state. The electron then drops to 2nd Bohr orbit. What is the frequency of radiation emitted and absorbed in the process ?

**SOLUTION :**

Energy is absorbed when electron moves from ground state ( $n = 1$ ) to 3rd excited state ( $n = 4$ ).

First calculate the energy difference between  $n = 1$  and  $n = 4$ .

$$\text{Use : } \Delta E_{(1 \rightarrow 4)} = 2.18 \times 10^{-18} \times Z^2 \times \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right);$$



Here  $Z = 1, n_1 = 1, n_2 = 4$

$$\Rightarrow \Delta E_{(1 \rightarrow 4)} = 2.18 \times 10^{-18} \times 1^2 \times \left( \frac{1}{1^2} - \frac{1}{4^2} \right) \text{J}$$

$$= 2.04 \times 10^{-18} \text{J}$$

This is the energy of the photon absorbed.

Use :  $E_{\text{photon}} = h\nu = 2.04 \times 10^{-18} \text{J}$  to get :

$$\Rightarrow \nu = 3.08 \times 10^{15} \text{ Hz}$$

- Similarly, when electron jumps from  $n = 4$  to  $n = 2$ , energy is emitted and is given by the same relation.

Put  $n_1 = 2$  and  $n_2 = 4$  in the expression of  $\Delta E$ , to get :

$$\Delta E_{(4 \rightarrow 2)} = 2.18 \times 10^{-18} \times 1^2 \times \left( \frac{1}{2^2} - \frac{1}{4^2} \right) \text{J}$$

$$= 4.08 \times 10^{-19} \text{J}$$

This is the energy of the photon emitted.

Use :  $E_{\text{photon}} = h\nu = 4.08 \times 10^{-19} \text{J}$

$$\Rightarrow \nu = 6.16 \times 10^{14} \text{ Hz}$$

**Example - 3** A hydrogen like ion,  $\text{He}^+$  ( $Z = 2$ ) is exposed to electromagnetic waves of  $256.2 \text{ \AA}$ . The excited electron gives out induced radiations. Find the wavelength of the induced radiations, when electron de-excites back to the ground state.  $R = 109737 \text{ cm}^{-1}$ .

#### SOLUTION :

$\text{He}^+$  ion contains only one electron, so Bohr's model is applicable here. It absorbs a photon of wavelength  $\lambda = 256.4 \text{ \AA}$ . Assume the electron to be in ground state initially. Let it jumps to an excited state  $n_2$ .

Use the relation, to find  $n_2$ .

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Substitute for  $\lambda = 256.2 \text{ \AA} = 256.2 \times 10^{-8} \text{ cm}$ ,

$R = 109737, Z = 2$  for  $\text{He}^+$  ion,  $n_1 = 1$

Now, Find  $n_2$ .

$$\frac{1}{256.2 \times 10^{-8}} = 109737 \times (2)^2 \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow n_2 = 3$$

From  $n = 3$ , the electron can fall back to the ground state in three possible ways (transitions) :

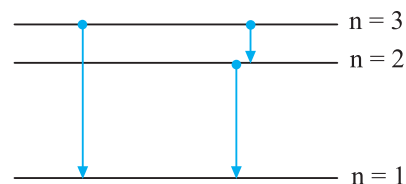
$$3 \rightarrow 1, \quad 3 \rightarrow 2, \quad 2 \rightarrow 1$$

Hence three possible radiations are emitted. Find the wavelengths corresponding to these transitions.

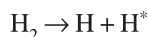
The wavelength ( $\lambda$ ) for transition,  $3 \rightarrow 1$  will be same i.e.,  $256.4 \text{ \AA}$ . Find  $\lambda$  for  $3 \rightarrow 2$  and  $2 \rightarrow 1$  using the same relation.

$$\lambda(3 \rightarrow 1) = 256.4 \text{ \AA}, \lambda(3 \rightarrow 2) = 1641.3 \text{ \AA},$$

$$\lambda(2 \rightarrow 1) = 303.9 \text{ \AA}$$



**Example - 4** Hydrogen gas when subjected to photo-dissociation, yields one normal atom and one atom possessing  $1.97 \text{ eV}$  more energy than normal atom. The bond dissociation energy of hydrogen molecule into normal atoms is  $103 \text{ kcal mol}^{-1}$ . Compute the wave length of effective photon for photo dissociation of hydrogen molecule in the given case.

**SOLUTION :**

where H is normal H-atom and  $\text{H}^*$  is excited H-atom.

So the energy required to dissociate  $\text{H}_2$  in this manner will be greater than the usual bond energy of  $\text{H}_2$  molecule.

$$E(\text{absorbed}) = \text{dissociation energy of } \text{H}_2 + \text{extra energy of excited atom}$$

Energy required to dissociate in normal manner

$$\begin{aligned} &= 103 \times 10^3 \text{ cal per mol} \quad (\text{given}) \\ &= \frac{103 \times 10^3 \times 4.18}{6 \times 10^{23}} = 7.17 \times 10^{-19} \text{ J/molecule} \end{aligned}$$

The extra energy possessed by excited atom is 1.97 eV

$$\equiv 1.97 \times 1.6 \times 10^{-19} \text{ J} = 3.15 \times 10^{-19} \text{ J}$$

$$\begin{aligned} E(\text{absorbed}) &= 7.175 \times 10^{-19} + 3.15 \times 10^{-19} \text{ J} \\ &= 1.03 \times 10^{-18} \text{ J} \end{aligned}$$

Now calculate the wavelength of photon corresponding to this energy.

$$\begin{aligned} E_{\text{photon}} &= \frac{hc}{\lambda} = 1.03 \times 10^{-18} \text{ J} \\ \Rightarrow \lambda &= 1930 \text{ \AA} \end{aligned}$$

**Example - 5**

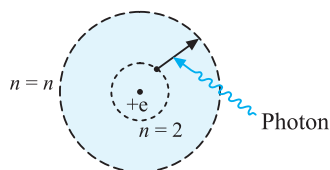
An electron in the first excited state of H-atom absorbs a photon and is further excited. The de Broglie wavelength of the electron in this state is found to 13.4 Å. Find the wavelength of photon absorbed by the electron in Å. Also find the longest and shortest wavelength emitted when this electron de-excites back to ground state.

**SOLUTION :**

**Note :** The energy state  $n = 1$  is known as Ground State  
The energy state  $n = 2$  is known as First Excited State.  
The energy state  $n = 3$  is known as Second excited State and so on.

The electron from  $n = 2$  absorbs a photon and is further excited to a higher energy level (let us say  $n$ ).

The electron in this energy level ( $n$ ) has a de Broglie wavelength ( $\lambda$ ) = 13.4 Å.



$$\lambda_e = \frac{h}{m_e v_e}$$

and  $v_e = 2.18 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$

[ $v_e$  is the velocity of  $e^-$  in  $n$ th Bohr orbit]

$$\begin{aligned} \Rightarrow v_e &= \frac{h}{\lambda m} = 2.18 \times 10^6 \left( \frac{1}{n} \right) \\ \Rightarrow \frac{6.626 \times 10^{-34}}{(13.4 \times 10^{-10}) \times (9.1 \times 10^{-31})} &= 2.18 \times 10^6 \times \frac{1}{n} \\ \Rightarrow n &= 4 \end{aligned}$$

Now find the wavelength of the photon responsible for the excitation from  $n = 2$  to  $n = 4$

Using the relation :

$$\begin{aligned} \Delta E_{(2 \rightarrow 4)} &= 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV} \\ &= 2.55 \text{ eV} \quad [n_1 = 2, n_2 = 4, Z = 1] \\ \Rightarrow \Delta E_{(2 \rightarrow 4)} &= \frac{12400}{\lambda \text{ (in \AA)}} \text{ eV} \\ \Rightarrow \lambda &= \frac{12400}{2.55} \text{ \AA} = 4863.1 \text{ \AA} \end{aligned}$$



The longest wavelength emitted when this electron (from  $n = 4$ ) falls back to the ground state will corresponds to the minimum energy transition.

The transition corresponding to minimum energy will be  $4 \rightarrow 3$ .

**Note:** The transition corresponding to maximum energy will be  $4 \rightarrow 1$ .

$$\Delta E_{(\text{Energy diff.})} = E_{\text{Photon}} = \frac{hc}{\lambda} = h\nu$$

$$\Rightarrow \Delta E \propto \frac{1}{\lambda_{\text{Photon}}} \text{ or } \Delta E \propto \nu_{\text{Photon}}$$

Using the same relation :

$$\Delta E_{(4 \rightarrow 3)} = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{eV}$$

$$[n_1 = 3, n_2 = 4, Z = 1]$$

$$\Rightarrow \Delta E_{(4 \rightarrow 3)} = 0.66 \text{ eV}$$

$$\Delta E = E_{\text{Photon}} = \frac{12400}{\lambda \text{ (in } \text{\AA})} \text{ eV}$$

$$\Rightarrow \lambda = 18752.8 \text{ \AA}$$

Shortest wavelength :  $4 \rightarrow 1$

$$\begin{aligned} \Delta E_{(4 \rightarrow 1)} &= 13.6 \times 1^2 \times \left( \frac{1}{1^2} - \frac{1}{4^2} \right) \text{eV} \\ &= 12.75 \text{ eV} \end{aligned}$$

$$\Rightarrow \Delta E_{(4 \rightarrow 1)} = E_{\text{Photon}} = \frac{12400}{\lambda \text{ (in } \text{\AA})} \text{ eV}$$

$$\Rightarrow \lambda = 973.2 \text{ \AA}$$

### Example - 6

A single electron orbits around a stationary nucleus of charge  $+Ze$ , where  $Z$  is a constant and  $e$  is the magnitude of electronic charge. It requires 47.2 eV to excite the electron from second Bohr orbit to the third Bohr. Find :

- the value of  $Z$
- the energy required to excite the electron from  $n = 3$  to  $n = 4$
- the wavelength of radiation required to remove electron from 2nd Bohr's orbit to infinity
- the kinetic energy, potential energy and angular momentum of the electron in the first orbit.
- the ionisation energy of above one electron system in eV.

### SOLUTION :

Since the nucleus has a charge  $+Ze$ , the atomic number of the ion is ' $Z$ '.

- (a) The transition is  $n_1 = 2 \rightarrow n_2 = 3$  by absorbing a photon of energy 47.2 eV.

$$\Rightarrow \Delta E = 47.2 \text{ eV}$$

Using the relation :

$$\Delta E = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{eV}$$

$$\Rightarrow 47.2 = 13.6 Z^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \Rightarrow Z = 5$$

- (b) The required transition is  $n_1 = 3 \rightarrow n_2 = 4$  by absorbing a photon of energy  $\Delta E$ .

Find  $\Delta E$  by using the relation :

$$\Delta E = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{eV}$$

$$\Rightarrow \Delta E = 13.6 (5)^2 \left( \frac{1}{3^2} - \frac{1}{4^2} \right) \text{eV}$$

$$\Rightarrow \Delta E = 16.53 \text{ eV}$$

- (c) The required transition is  $n_1 = 2 \rightarrow n_2 = \infty$  by absorbing a photon of energy  $\Delta E$ .

Find  $\Delta E$  by using the relation :

$$\Delta E = 13.6 (5)^2 \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \Rightarrow \Delta E = 85 \text{ eV}$$

Find  $\lambda$  of radiation corresponding to energy 85 eV.

$$\Rightarrow \lambda = \frac{12400}{85} \text{ \AA} \\ = 146.16 \text{ \AA}$$

- (d) If energy of electron be  $E_n$ , then  $KE = -E_n$  and  $PE = 2E_n$

$$E_n = \frac{-13.6 Z^2}{n^2} = \frac{-13.6 \times 5^2}{1^2} = -340 \text{ eV}$$

$$KE = -(-340 \text{ eV}) = 340 \text{ eV}$$

$$PE = 2(-340 \text{ eV}) = -680 \text{ eV}$$

$$\text{Angular momentum } (\ell) = n \left( \frac{h}{2\pi} \right)$$

$$\Rightarrow \ell = 1 \times \left( \frac{6.626 \times 10^{-34}}{2\pi} \right) \\ = 1.05 \times 10^{-34} \text{ J-s}$$

**Note :** Angular momentum of  $e^-$  is also equal to  $m_e v_e r$ .

- (e) The ionisation energy (IE) is the energy required to remove the electron from ground state to infinity. So the required transition is  $1 \rightarrow \infty$ . The ionisation energy (IE)  $= -E_1 = 13.6 (Z)^2 \text{ eV}$   
 $\Rightarrow 1E = +13.6 \times 5^2 = 340 \text{ eV}$ .

### Example - 7

The hydrogen-like species  $Li^{2+}$  is in a spherically symmetric state  $S_1$  with one radial node. Upon absorbing light the ion undergoes transition to a state  $S_2$ . The state  $S_2$  has one radial node and its energy is equal to the ground state energy of the H-atom.

- (i) The state  $S_1$  is :

- (A) 1s (B) 2s  
(C) 2p (D) 3s

- (ii) Energy of the state  $S_1$  in units of the hydrogen atom ground state energy is :

- (A) 0.75 (B) 1.50  
(C) 2.25 (D) 4.50

- (iii) The orbital angular momentum quantum number of the state  $S_2$  is :

- (A) 0 (B) 1  
(C) 2 (D) 3

**SOLUTION :** (i)-(B) (ii)-(C) (iii)-(B)

Radial node  $= n - \ell - 1$

$S_1 \equiv 2s$  (As it is spherically symmetric and has one radial node)

$S_2 \equiv 3p$  (As its energy is equal to ground state energy of H-atom hence, its principal quantum number is 3 and it contains only 1 radial node)

Hence its Orbital angular momentum quantum number is 1. ( $1 = 3 - \ell - 1 \Rightarrow \ell = 1$ )

Energy of electron in  $S_1$

$$= -13.6 \times \frac{Z^2}{n^2} \text{ eV} = -13.6 \times \frac{3^2}{2^2} \text{ eV}$$

Energy of hydrogen in ground state  $= -13.6 \text{ eV}$

$\Rightarrow$  Energy of electron in  $S_1$  is 2.55 times the energy hydrogen atom in ground state.

### Example - 8

Find the energy required to excite 1.10 litre of hydrogen atoms gas at 1.0 atm and 298 K to the first excited state of atomic hydrogen. The energy required for the dissociation of H-H bond is 436 kJ/mol. Also calculate the minimum frequency of a photon to break this bond.

**SOLUTION :**

Let us, first find the number of moles of hydrogen atoms.

$$n_{H_2} = \frac{PV}{RT} = \frac{1 \times 1.10}{0.0821 \times 298} = 0.045$$

Thus the energy required to break 0.045 moles of  $H_2$  (H–H bond) =  $0.045 \times 436 = 19.62$  kJ.

Now calculate the energy needed to excite the H-atoms to first excited state i.e., to  $n = 2$  (First excited state is referred to  $n = 2$ ).

$$\Delta E = 2.18 \times 10^{-18} (1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \text{ J/atom}$$

$$= 1.635 \times 10^{-18} \text{ J/atom}$$

$$\text{No. of H atoms} = (\text{No. of } H_2 \text{ molecules}) \times 2$$

$$= (0.05 \times 6.02 \times 10^{23}) \times 2 = 6.02 \times 10^{22}$$

The energy required to excite the given number of H-atoms =  $6.02 \times 10^{22} \times 1.635 \times 10^{-18} \text{ J} = 98.43$  kJ

So the total energy required

$$= 19.62 + 98.43 = 118.05 \text{ kJ}$$

Now the energy required to break a single

$$\text{H-H bond} = \frac{436 \times 10^3}{6.023 \times 10^{23}} = 7.238 \times 10^{-19} \text{ J/atom}$$

= Energy supplied by the photon

$$\Rightarrow 7.238 \times 10^{-19} = h\nu = 6.626 \times 10^{-34} (\nu)$$

$$\Rightarrow \nu = 1.09 \times 10^{15} \text{ Hz.}$$

**Example - 9**

Estimate the difference in energy between 1st and 2nd Bohr's orbit for a H-atom. At what minimum atomic number (Z), a transition from  $n = 2$  to  $n = 1$  energy level would result in the emission of radiation with wavelength  $\lambda = 3.0 \times 10^{-8} \text{ m}$ ? Which Hydrogen atom like species this atomic number corresponds to? How much ionisation potential is needed to ionise this species? ( $R = 1.097 \times 10^7 \text{ m}^{-1}$ )

**SOLUTION :**

The difference in energy is given by  $\Delta E$  :

$$\Delta E = 2.18 \times 10^{-18} (1)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \text{ J/atom}$$

$$= 1.65 \times 10^{-18} \text{ J} \equiv 1.65 \times 10^{-11} \text{ ergs} \equiv 10.2 \text{ eV}$$

For a H-like atom,  $\lambda = 3.0 \times 10^{-8} \text{ m}$ .

$$\Rightarrow \frac{\Delta E}{(2 \rightarrow 1)} = 2.18 \times 10^{-18} \times Z^2 \times \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \text{ J}$$

$$= E_{\text{photon}} = \frac{hc}{\lambda} \Rightarrow Z = 2$$

Hence the H-like atom is  $He^+$  ion.

To ionise,  $He^+$  ion, ionisation energy (IE) =  $-(E_1)$

$$IE = -(-13.6 \times 2^2) = +54.4 \text{ eV}$$

The ionisation potential (IP) is the voltage difference required to generate this much energy.

$$\Rightarrow IE = qV = e(IP) = 54.4 \text{ eV}$$

$$\Rightarrow IP(\text{required}) = 54.4 \text{ Volts}$$

**Example - 10**

Match the following :

**List 1**

- (A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital  
(B) A hydrogen-like one-electron wave function obeying Pauli principle  
(C) Shape, size and orientation of hydrogen-like atomic orbitals  
(D) Probability density of electron at the nucleus in hydrogen-like atom

**List 2**

- (p) Principal quantum number  
(q) Azimuthal quantum number  
(r) Magnetic quantum number  
(s) Electron spin quantum number

**SOLUTION : [A-q, r] [B-p, q, r, s] [C-p, q, r] [D-p, q]**

- (A) Orbital angular momentum of the electron in a hydrogen like atomic orbital depends on type of atomic orbital ( $\ell$ ) and its orientation ( $m_\ell$ ).  
(B) As per Pauli's principle, every electron is unique, hence all four quantum numbers are required.

- (C) Shape, size and orientation of hydrogen-like atomic orbital are indicated by  $\ell$ ,  $n$ ,  $m_\ell$ .  
(D) Probability density of electron at the nucleus in hydrogen-like atom is obtained by the square of the wave functions. ( $\psi^2$ ) and it depends on  $n$  and  $\ell$

**Example - 11** A stationary  $\text{He}^+$  ion emits a photon corresponding to the first line ( $H_\alpha$ ) of Lyman series. The photon thus emitted, strikes a H-atom in the ground state. Find the velocity of the photoelectron ejected out of the hydrogen atom. The value of  $R = 1.097 \times 10^7 \text{ m}^{-1}$ .

**SOLUTION :**

The difference in energy ( $\Delta E$ ) will be equal to the energy of the photon emitted.

First line in Lyman series corresponds to the transition  $2 \rightarrow 1$ .

$$\Delta E = 2.18 \times 10^{-18} (2)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \text{ J/atom}$$

$$= 6.54 \times 10^{-18} \text{ J}$$

The photon of this much energy strikes a H-atom in the ground state. Note that the ionisation energy of H-atom is  $+2.18 \times 10^{-18} \text{ J}$ . This will be the work function of H-atom. Using the Einstein's photoelectric equation :

$$\text{KE} = E_i - W_o = \frac{1}{2} m_e v_e^2 \quad [E_i = \text{Incident energy}]$$

$$\Rightarrow v_e = \sqrt{\frac{2(E_i - W_o)}{m_e}}$$

$$\Rightarrow v_e = \sqrt{\frac{2(6.54 \times 10^{-18} - 2.18 \times 10^{-18})}{9.1 \times 10^{-31}}}$$

$$\Rightarrow v_e = 3.09 \times 10^6 \text{ m/s}$$

We can also calculate the wavelength of electron ejected out  $= 2.36 \times 10^{-10} \text{ m} \equiv 2.36 \text{ \AA}$

$$\lambda_e = \frac{h}{m_e v_e} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 3.09 \times 10^6} \text{ m} = 2.36 \text{ \AA}$$

**Example - 12** An electron in a hydrogen like species, makes a transition from  $n$ th Bohr orbit to next outer Bohr ( $\equiv n + 1$ ). Find an approximate relation between the dependence of the frequency of the photon absorbed as a function of ' $n$ '. Assume ' $n$ ' to be a large value ( $n \gg 1$ ).

**SOLUTION :**

$$\Delta E_{\text{(energy difference)}} = h\nu = 2.18 \times 10^{-18} \times Z^2 \left( \frac{1}{n^2} - \frac{1}{(n+1)^2} \right) \text{ J}$$

( $n \rightarrow n+1$ )

$$\Rightarrow h\nu = 2.18 \times 10^{-18} \times Z^2 \left( \frac{2n+1}{n^2(n+1)^2} \right) \text{ J}$$

Since  $n \gg 1$  (given)

$$\Rightarrow n+1 \sim n; 2n+1 \approx 2n$$

$$\Rightarrow h\nu \approx 2.18 \times 10^{-18} Z^2 \times \frac{2n}{n^4} \text{ J} \quad \Rightarrow \nu \propto n^{-3}$$

## MISCELLANEOUS EXERCISE

Choose the correct options for each of the following questions. Questions marked with \* may have more than one correct options.

- If a certain metal was irradiated by using two different light radiations of frequency ' $x$ ' and ' $2x$ ', the maximum kinetic energy of the ejected electrons are ' $y$ ' and ' $3y$ ' respectively. The threshold frequency of the metal is :  
(A)  $x/3$  (B)  $x/2$  (C)  $3x/2$  (D)  $2x/3$
- A hydrogen atom in a state having a binding energy of 0.85 eV makes a transition to a state with excitation energy 10.2 eV. The energy in (eV) of the emitted photon is :  
(A) 2.55 (B) 5.1 (C) 3.85 (D) 12.75
- \*3. The energy of an electron in the Bohr's first orbit of H-atom is -13.6 eV. The possible energy values in (eV) of the excited states for electron in Bohr's orbits of hydrogen is(are) :  
(A) -3.4 (B) -4.2 (C) -6.8 (D) +6.8
- Ratio of frequency of revolution of electron in the 2nd excited state of  $\text{He}^+$  and 2nd state of hydrogen is :  
(A)  $32/27$  (B)  $27/32$   
(C)  $1/54$  (D)  $27/2$
- The wavelength of the first line of Lyman series for hydrogen is identical to that of the second line of Balmer series for some hydrogen like ion ' $X$ '. The  $E_2$  for ' $X$ ' is :  
(A) -54.4 eV (B) -32.8 eV  
(C) -13.6 eV (D) -3.8 eV
- If each hydrogen atom in the ground state of 1.0 mol of H-atoms is excited by absorbing photons of energy 8.4 eV, 12.09 eV and 15.0 eV of energy, then the number of spectral lines emitted is equal to :  
(A) None (B) Two  
(C) Three (D) Four
- \*7. When an electron of H-atom jumps from a higher to lower energy state, then :  
(A) its potential energy decreases  
(B) its kinetic energy increases  
(C) its angular momentum remains unchanged  
(D) wavelength of de Broglie wave associated with the electron decreases

## For Q. 8 - 10

In a mixture of H –  $\text{He}^+$  gas ( $\text{He}^+$  is singly ionized He atom), H atoms and  $\text{He}^+$  ions are excited to their respective first excited states. Subsequently, H atoms transfer their total excitation energy to  $\text{He}^+$  ions (by collisions). Assuming that the Bohr model of atom is applicable, answer the following questions.

- The quantum number  $n$  of the state finally populated in  $\text{He}^+$  ions is :  
(A) 2 (B) 3 (C) 4 (D) 5
- The wavelength of light emitted in the visible region by  $\text{He}^+$  ions after collisions with H atoms is :  
(A)  $6.5 \times 10^{-7} \text{ m}$  (B)  $5.6 \times 10^{-7} \text{ m}$   
(C)  $4.8 \times 10^{-7} \text{ m}$  (D)  $4.0 \times 10^{-7} \text{ m}$
- The ratio of the potential energy of the  $n = 2$  electron for the H atom to that of  $\text{He}^+$  ion is :  
(A)  $1/4$  (B)  $1/2$  (C) 1 (D) 2
- \*11. In a hydrogen like species, electron is in 2nd excited state. The Binding energy of 4th state of this species is 13.6 eV, then :  
(A) A 25 eV photon can set free the electron from the second excited state of this sample  
(B) 3 different types of photon will be observed if electron make transition up to ground state from the second excited state  
(C) If 23 eV photon is used for electron in 2nd excited state then K.E. of the ejected electron is 1 eV  
(D) 2nd line of Balmer series of this sample has same energy value as 1st excitation energy of H-atoms
- \*12. The ratio of the de Broglie wavelength of a proton and  $\alpha$ -particles will be 1 : 2 if their :  
(A) velocity are in the ratio 1 : 8  
(B) velocity are in the ratio 8 : 1  
(C) kinetic energy are in the ratio 1 : 64  
(D) kinetic energy are in the ratio 1 : 256

13. Which of the following has the maximum number of unpaired electrons ?  
 (A)  $\text{Mg}^{2+}$  (B)  $\text{Ti}^{3+}$  (C)  $\text{V}^{3+}$  (D)  $\text{Fe}^{2+}$
- \*14. Which of the following statements is (are) incorrect for an electron of quantum numbers  $n = 4$  and  $m = 2$  ?  
 (A) The value of  $\ell$  may be 2  
 (B) The value of  $\ell$  may be 3  
 (C) The value of  $s$  may be  $+1/2$   
 (D) The value of  $\ell$  may be 0, 1, 2, 3.
- \*15. Pick out the orbitals with the maximum number of nodal planes ?  
 (A)  $3d_{xy}$  (B)  $4d_{z^2}$  (C)  $4d_{xy}$  (D)  $2p_x$
16. Which of the following orbitals will have the maximum number of radial nodes ?  
 (A)  $3s$  (B)  $4d_{z^2}$  (C)  $4d_{xy}$  (D)  $2p_x$
- For Q. 17 - 18**  
 It is impossible to determine simultaneously the position of velocity of small microscopic particle like, electron, proton or neutron with accuracy. This is called Heisenberg's uncertainty principle. Mathematically it is represented as  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$   
 $\Delta x$  is uncertainty in position,  $\Delta p$  is uncertainty in momentum.
17. If uncertainty in the measurement of position and momentum of an electron are equal then uncertainty in the measurement of its velocity is approximately :  
 (A)  $8 \times 10^{12} \text{ m/s}$  (B)  $6 \times 10^{12} \text{ m/s}$   
 (C)  $4 \times 10^{12} \text{ m/s}$  (D)  $2 \times 10^{12} \text{ m/s}$
18. If a 1.0 g body is travelling along X-axis at  $100 \text{ cm s}^{-1}$  with an uncertainty in velocity as  $2 \text{ cm s}^{-1}$ . The uncertainty in its position is :  
 (A)  $5.28 \times 10^{-30} \text{ m}$  (B)  $2.64 \times 10^{-30} \text{ m}$   
 (C)  $1.30 \times 10^{-30} \text{ m}$  (D)  $0.66 \times 10^{-30} \text{ m}$
19. A mono chromatic source of light rated at 200 W emits  $4 \times 10^{20}$  photons per second. Find the wavelength of light.  
 (A) 400 nm (B) 800 nm  
 (C) 1200 nm (D) None of these
20. Three photons coming from excited atomic-hydrogen sample are picked up. Their energies are 12.1 eV, 10.2 eV and 1.9 eV. These photons must come from :  
 (A) a single atom (B) two atoms  
 (C) three atoms (D) either two atoms or three atoms
21. In which of the following transitions will the wavelength be minimum ?  
 (A)  $n = 5$  to  $n = 4$  (B)  $n = 4$  to  $n = 3$   
 (C)  $n = 3$  to  $n = 2$  (D)  $n = 2$  to  $n = 1$
22. If the shortest wavelength of H-atom in Lyman series is  $x$ , then longest wavelength in Balmer series of  $\text{He}^+$  is :  
 (A)  $\frac{9x}{5}$  (B)  $\frac{36x}{5}$  (C)  $\frac{x}{4}$  (D)  $\frac{5x}{9}$
- \*23. Which of the following relate to light as wave motion ?  
 (A) diffraction (B) interference  
 (C) photoelectric effect (D)  $E = mc^2$

24. Match the entries in Column I with the correctly related quantities in Column II.

**Column - I (Electronic transition)**

- (A)  $n_1 \rightarrow n_\infty$  in H-atoms  
 (B)  $n_4 \rightarrow n_2$  in  $\text{He}^+$  ion  
 (C)  $n_\infty \rightarrow n_1$  in  $\text{He}^+$  ion  
 (D)  $n_4 \rightarrow n_2$  in H-atom

**Column - II (Characteristics of radiation concerned)**

1. Visible radiations  
 2. Energy numerically equal to Rydberg energy  
 3. Energy numerically equal to Ionization Energy  
 4. Ultraviolet radiations

25. Match the entries in Column I with the correctly related quantities in Column II.

**Column - I**

- (A) Angular momentum  
 (B) Kinetic energy  
 (C) Potential energy  
 (D) Velocity

**Column - II**

1. Increases by increasing  $n$   
 2. Decreases by decreasing  $Z$   
 3. Increases by decreasing  $Z$   
 4. Decreases by decreasing  $n$

## ANSWERS TO IN-CHAPTER EXERCISES

A	1. 28	2. 1.03 eV	3. 3.9 eV	4. $4.77 \times 10^{-18} \text{ J}$	5. 4	6. B
	7. C	8. D	9. B	10. B	11. C	12. C
B	1. 405.2 Å	2. $2 \rightarrow 1$	3. $n = 5$	4. 24.18 eV	5. 4862.76 Å	
	6.(a) 3647.07 Å	(b) $2.18 \times 10^{-18} \text{ J}$	(c) 911.8 Å	7. $1.05 \times 10^{15} \text{ Hz}$	8. BC	9. C
	10. C	11. C	12. A	13. B	14. B	15. D
	16. ABD	17. D	18. BC	19. D	20. A	21. ABC
	22. A	23. D	24. D	25. C	26. A	27. A
	28. B	29. A				
C	1. 12.26 Å	2. $10^{-7} \text{ m}$				
	4.(a) $2p_x$ or $2p_y$	(b) $4d_{z^2}$	(c) $3p_z$	(d) $3d_{xy}$ or $3d_{x^2-y^2}$	(e) $4p_x$ and $4p_y$	
	7. $4s : 0$	$3p : \frac{\sqrt{2}h}{2\pi}$	$3d : \frac{\sqrt{6}h}{2\pi}$	8. $5.8 \times 10^5 \text{ m/s}$	9. B	10. D
	11. C	12. C	13. A	14. A	15. C	16. A
	17. B	18. C	19. C	20. D	21. D	22. C
	23. C	24. D	25. A	26. A	27. A	

## ANSWERS TO MISCELLANEOUS EXERCISE

1. B	2. A	3. A	4. A	5. C	6. C
7. ABD	8. C	9. C	10. A	11. AB	12. B
13. D	14. D	15. AC	16. A	17. A	18. B
19. A	20. D	21. D	22. A	23. AB	
24. [A-2, 3, 4] [B-4] [C-1, 3, 4] [D-1]			25. [A-1, 4] [B-2] [C-1, 3, 4] [D-2]		